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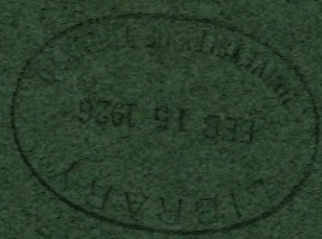
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**SAMPLING AND EXAMINATION
OF MINE GASES AND
NATURAL GAS**

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HERBERT HOOVER, SECRETARY

BUREAU OF MINES

SCOTT TURNER, DIRECTOR

SAMPLING AND EXAMINATION
OF MINE GASES AND NATURAL GAS

A REVISION OF BULLETIN 42

BY

GEORGE A. BURRELL AND FRANK M. SEIBERT

REVISED BY G. W. JONES



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SAMPLING AND EXAMINATION OF MINE GASES AND NATURAL GAS

By GEORGE A. BURRELL and FRANK M. SEIBERT; revised by
G. W. JONES

FOREWORD

In this bulletin, the style of Bulletin 42 has been closely followed. Much of the material is reprinted on the following pages in its original form, and changes have been made only where manifestly necessary. Laboratory methods have been brought up to date. Some types of apparatus described in Bulletin 42 have now become obsolete and newer designs are described instead. The authors hope that this bulletin will be of as much service as was Bulletin 42.

ACKNOWLEDGMENTS

Revision has necessitated the inclusion of data that have been published within the last few years. Proper credit is always given the authors of such material by references to the original articles. The reviewer especially acknowledges his use of information taken from papers prepared by R. R. Sayers, W. P. Yant, G. G. Oberfell, M. C. Teague, I. W. Robertson, F. N. Neumeister, W. C. Harpster, W. L. Parker, S. H. Katz, J. D. Davis, and A. C. Fieldner.

INTRODUCTION TO BULLETIN 42

The Bureau of Mines, as part of its designated duty of investigating the causes of mine accidents, is conducting at its experiment station in Pittsburgh, Pa., a study of mine gases. Some of the work already done in connection with this study is outlined below.

A large number of samples of mine gas have been collected under normal conditions in returns and in splits, and at other points in the ventilating current; also at the face, in the goave or gob, in unventilated places, and wherever the air was still.¹ Samples have also been obtained under abnormal conditions, as after explosions and while mine fires were in progress, or from sealed areas behind stoppings and dams where the air had been stagnant for some time.

¹ Burrell, G. A., Robertson, I. W., and Oberfell, G. G., Black damp in mines: Bull. 105, Bureau of Mines, 1916, 92 pp.

Chemical changes in the composition of mine atmospheres during mine fires have been studied,² and conditions peculiar to certain mines have been investigated.

The effect of a change in atmospheric pressure on the escape of gas (methane) in coal mines has been studied. Explosives have been fired in both coal and metal mines, and samples of resulting gases have been collected to ascertain the degree to which these vitiate the air. A series of samples in mines where gasoline locomotives were being used has been examined in order to ascertain the degree to which the exhaust gases from such locomotives foul the air.³ Experiments have also been made in regard to the relative effect of carbon monoxide upon men and small animals,⁴ the effect of oxygen deficiency on men and animals,⁵ and the flammable limits of combustible gases found normally in mines and during and after mine fires.⁶

These investigations have necessitated making numerous gas analyses, many requiring special methods and designs of apparatus. The methods described herein are largely an outgrowth of the above investigations and are now used as standard methods at the gas laboratory of the Pittsburgh station of the Bureau of Mines.

COLLECTION OF SAMPLES OF MINE GASES

SAMPLING BY THE VACUUM METHOD

In nearly all mines where there is enough air movement—say, a velocity of at least 100 feet per minute—samples of atmospheres are taken by the vacuum-bulb method. Glass bulbs of about 250-c.c. capacity (2 by 6 inches in size) are made at the Pittsburgh experiment station of the Bureau of Mines. As these bulbs are made they are evacuated as completely as possible by a high-vacuum pump, and the long capillary neck is sealed with a flame during the final stage of evacuation. Then the bulbs are labeled and numbered and are ready

² Burrell, G. A., and Seibert, F. M., Gas analysis as an aid in fighting mine fires: Tech. Paper 13, Bureau of Mines, 1912, 16 pp.

³ Hood, O. P., and Kudlich, R. H., Gasoline mine locomotives in relation to safety and health: Bull. 74, Bureau of Mines, 1915, 84 pp.

⁴ Burrell, G. A., Seibert, F. M., and Robertson, I. W., Relative effects of carbon monoxide on small animals: Tech. Paper 62, Bureau of Mines, 1914, 23 pp.

⁵ Burrell, G. A., and Oberfell, G. G., Effects of oxygen deficiency on small animals and on men: Tech. Paper 122, Bureau of Mines, 1915, 12 pp.

⁶ Burrell, G. A., and Seibert, F. M., The inflammable gases in mine air: Tech. Paper 39, Bureau of Mines, 1913, 24 pp. Burrell, G. A., and Oberfell, G. G., The limits of inflammability of mixtures of methane and air: Tech. Paper 119, Bureau of Mines, 1915, 30 pp.; Explosibility of gases from mine fires: Tech. Paper 134, Bureau of Mines, 1916, 31 pp.; The explosibility of acetylene: Tech. Paper 112, Bureau of Mines, 1915, 15 pp. Burrell, G. A., and Robertson, I. W., Effects of temperature and pressure on the explosibility of methane-air mixtures: Tech. Paper 121, Bureau of Mines, 1916, 14 pp. Burrell, G. A., and Gauger, A. W., Limits of complete inflammability of mixtures of mine gases and of industrial gases with air: Tech. Paper 150, Bureau of Mines, 1917, 13 pp.

for shipment to engineers in the field. The shipping containers are wooden boxes (11 by 7½ by 4½ inches, outside measurement) which have two compartments lined with corrugated paper board to minimize the possibility of breakage during shipment, and are of a size to be shipped by parcel post. Figure 1 shows a box containing two vacuum bulbs. When the samples have been taken the bulbs are wrapped in paper so as to fit snugly in the compartments, and more paper is packed around the necks. Each compartment contains a form card on which information can be noted. Definite directions for sampling gases by the vacuum-bulb method can not be given to fit all circumstances, because of the many varying conditions encountered in different mines or even in different parts of the same mine. It must be understood that the vacuum bulb takes a sample of gas at one point only—where the tip of the bulb is broken off. This condition largely limits its use to these places where there is enough air movement to make the composition of the gases uniform across a given cross section in a return airway or entry.

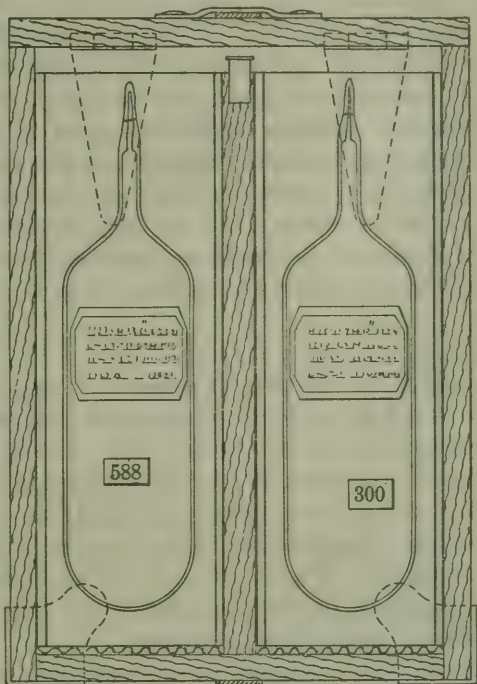


FIGURE 1.—Shipping box containing vacuum bulbs

SAMPLING WHERE THERE IS APPRECIABLE AIR MOVEMENT

To sample where there is appreciable air movement, stand facing the direction of air movement—that is, with the air blowing against the face—and hold the vacuum bulb, with arms outstretched (to prevent contamination of the sample with expired air from the breath), as nearly as possible in the center of the place to be sampled. While the bulb is held in this position, break off the end of the capillary tube at a file mark or scratch thereon. When a file scratch has been made at the desired place, glass tubing is easily broken by holding the tube with one hand on each side of the file mark with the mark facing upward and pressing down slightly on each side of the mark. A small piece of wood with a small hole

bored at each end is included in the sampling outfit to provide a better handhold for the glass tube. Insert the latter in the deeper of the two holes almost up to the scratch; slight pressure downward will then break the tip. If a wooden plug is not available, use a small pair of pliers or slip the tube through the hole in the handle of a common cabinet lock key.

As soon as the tip is broken air rushes into the bulb; a few seconds later close the tube by forcing some specially prepared wax into the end broken. (Prepare the wax at the laboratory by heating two parts of beeswax with one part of Venice turpentine. During the warm summer months, or for the collection of samples in hot places in deep metal mines, increase the proportion of beeswax 20 per cent. Melt the wax and pour it into empty 38-caliber short brass cartridge shells, of which there are two in each shipping container.) Force a shell over the capillary opening for one-fourth to one-half inch.

Samples should always be taken in duplicate.

SAMPLING IN STILL AIR

If the vacuum-bulb method is used for sampling atmospheres that are not of uniform composition, take several samples across a cross section to get an average value for the given area. If the composition is thought to vary from bottom to top or from side to side, divide the cross section as nearly as can be judged by the eye into equal rectangles, and take a sample of the gas from the center of each rectangle. Under such conditions, where the composition of the gas is thought to vary, the number of samples taken on the cross section should not be less than four.

After the samples have been taken and notes recorded on the blue cards provided in the shipping box, replace the bulbs with the cards and mail them to the gas-analysis laboratory.

SAMPLING BY AIR DISPLACEMENT

There are some places in mines where sampling by the vacuum method is difficult, if not impossible, such as behind brattices built to confine an area during fires. To sample such places, fasten a rubber tube and a sufficiently long glass or small metal tube to the suction end of an aspirator bulb. Pass the tube through a small hole in the stopping and pack the hole tightly with clay or other suitable material. Place the other extension from the bulb in the sampling bottle; compress the bulb, forcing the air from behind the stopping into a magnesium citrate or other bottle used as a container. The authors have found that compressing the bulb 50 times more than suffices to replace completely the air in an 8-ounce bottle. When the air in the bottle has been entirely replaced with gas, withdraw the rubber tube slowly and close the bottle at once to prevent access of

air. A margin of safety is provided because the bulbs become less efficient with use, although their usefulness can be fairly well determined by compressing the bulb and closing one end to determine whether or not there is leakage. A little dust sometimes lodges on the valve seats.

SAMPLING BY WATER DISPLACEMENT

WATER AS DISPLACING FLUID

Water may be used as the displacing fluid in the collection of samples of air that are to be examined for methane only, because water has no appreciable absorbent action upon methane; but the content of carbon dioxide in a sample collected by this means will be less than actual. In order to show the loss of carbon dioxide the following experiments were performed:

Prepared mixtures of carbon dioxide and air were collected in clean bottles by water displacement and were analyzed daily for carbon dioxide. In collecting the samples the bottles were almost completely emptied of the water so that only a thin film remained on the inner side. The progressive decrease of the carbon dioxide within the bottles is shown as follows:

Decrease of CO₂ in a prepared mixture of CO₂ and air contained within bottles wet with distilled water

Day of analysis	Carbon dioxide, per cent	
	Sample 1	Sample 2
First.....	0.53	0.52
Second.....	.50	.49
Third.....	.46	.48
Fourth.....	.41	.44

The bottles (sample containers) had a capacity of about 300 c. c. It was found that after they had been drained of distilled water in the ordinary operation of collecting a sample, about 0.7 c. c. of the water still remained on the inner surface. The following calculation shows how small a quantity of carbon dioxide could be absorbed by this volume of pure water:

Pure water absorbs approximately its own volume of carbon dioxide at normal temperature and pressure, so the 0.7 c. c. of water remaining on the inside of these containers should absorb about 0.7 c. c. of carbon dioxide at normal pressure. The partial pressure of the carbon dioxide was 760×0.0053 , or 4 mm. The amount of carbon dioxide absorbed by the water becomes then $\frac{4 \times 0.7}{760} = 0.0036$ c. c., or 0.0012 per cent of the entire quantity of the gas sample.

This is within the error of making the analysis (0.01 per cent); hence the appreciable loss of carbon dioxide noted above must have been due to some other cause than absorption of carbon dioxide by water. It is probable that absorption of carbon dioxide in the alkali dissolved out of the glass by the water was responsible. Haldane⁷ has called attention to the absorption of carbon dioxide by alkali dissolved out of glass by water, and has pointed out that in a wet, dirty bottle an appreciable amount of carbon dioxide may appear and oxygen may disappear by bacterial action.

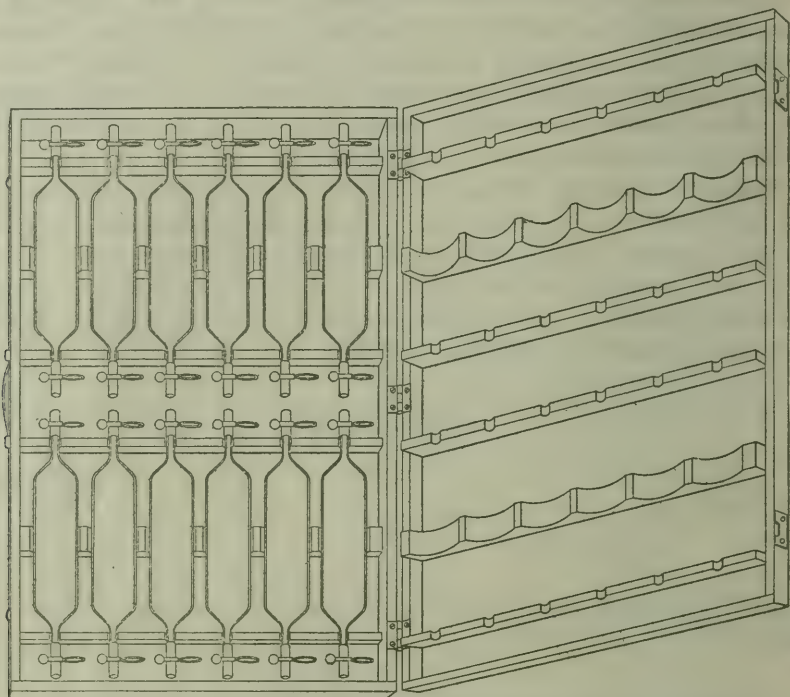


FIGURE 2.—Glass tubes for taking samples by water displacement

PROCEDURE FOR SAMPLING

Figure 2 shows twelve 250-c. c. glass sampling tubes assembled in a box. Before a sample of the gas is taken fill the tubes with water. Pinch clamps over short pieces of rubber tubing, make the tubes gas-tight, connect the upper end with the place where a sample of gas is to be taken, and open the pinch clamps; the water then flows out and draws in the sample of gas. When all of the water has run out, close the pinch clamps, and the sample is ready for analysis. Analyze samples taken by this method as soon as possible, because rubber tubing is not impervious to gases when left over a

⁷ Haldane, J. S., *Methods of air analysis*. 1912, p. 3.

long period. The box serves as a convenient means of carrying the sample containers to and from the laboratory. Each tube in the box is protected by strips of felt, and when the box is closed each is held firmly in place.

CHECKING THE READING OF A FLAME SAFETY LAMP

It is frequently desired to obtain samples of mine atmospheres to check the percentages of methane indicated by a flame safety lamp. To collect such a sample after the safety lamp has been "read," hold the bottle so that the point at which the mine atmosphere enters is close to the place where the air inlet of the safety lamp has been. If there is a still accumulation of methane and air, especially a pocket of gas near the roof, it is obvious that even with the greatest care some disturbance of the atmosphere will occur in sampling by some of the methods already mentioned, so that the sample collected in the container may not have exactly the same composition as the air that entered the lamp.

Minimum disturbance of the atmosphere will result if the sample is taken by the vacuum-bulb method, the bulb carefully raised to the place to be sampled, and the tip broken with care.

DETERMINATION OF MOISTURE

USE OF WET AND DRY BULB THERMOMETERS

Plate I shows the wet and dry bulb thermometers (psychrometer) used by the Bureau of Mines for determining the amount of moisture in the air. The thermometers are mounted as a unit in an aluminum frame. Opposite the thermometer bulbs are slots to allow free circulation of air. To use the hygrometer, remove the leather case, hold the apparatus firmly by the handle shown, and swing it in a circular path facing the air current.

To make standard readings with the hygrometer, or sling psychrometer, described above, the speed of the revolving bulb must be about 15 feet per second. Whirl the psychrometer for 15 or 20 seconds and then read it, the wet bulb first. Repeat this process until successive readings agree closely.

The relative humidity of the atmosphere can be determined from the wet and dry bulb for different observations of barometric pressure by the psychrometric tables⁸ issued by the Weather Bureau.

Figures 3 and 4 show curves⁹ from which the relative humidity of a mine atmosphere can be found from the wet and dry bulb read-

⁸ Marvin, C. F., Psychrometric tables for obtaining the vapor pressure, relative humidity, and temperature of the dew point: Dept. of Agriculture, Weather Bureau Bull. 235, 1910, 84 pp.

⁹ Rice, G. S., The explosibility of coal dust: Bull. 20, Bureau of Mines, 1911, pp. 59 and 66.

ings when the pressure is 30 inches of mercury; also the number of gallons of water equivalent to the same weight of water vapor in

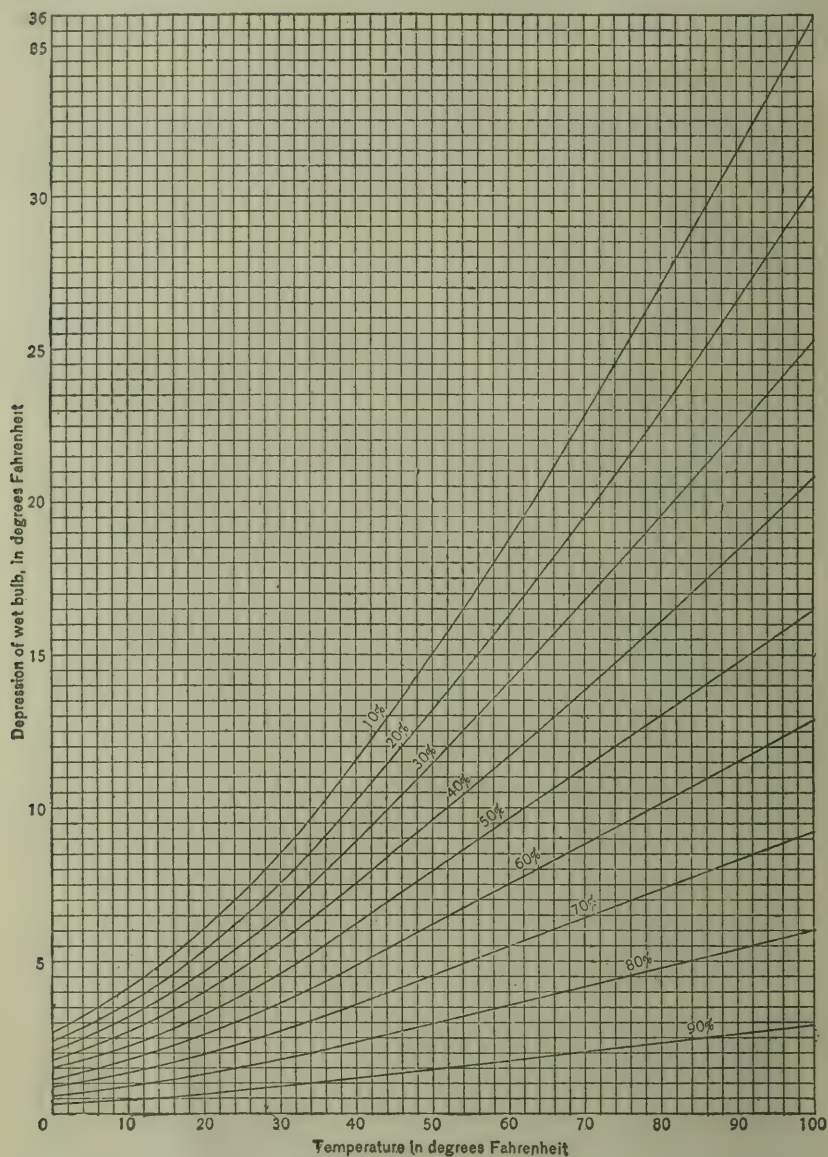
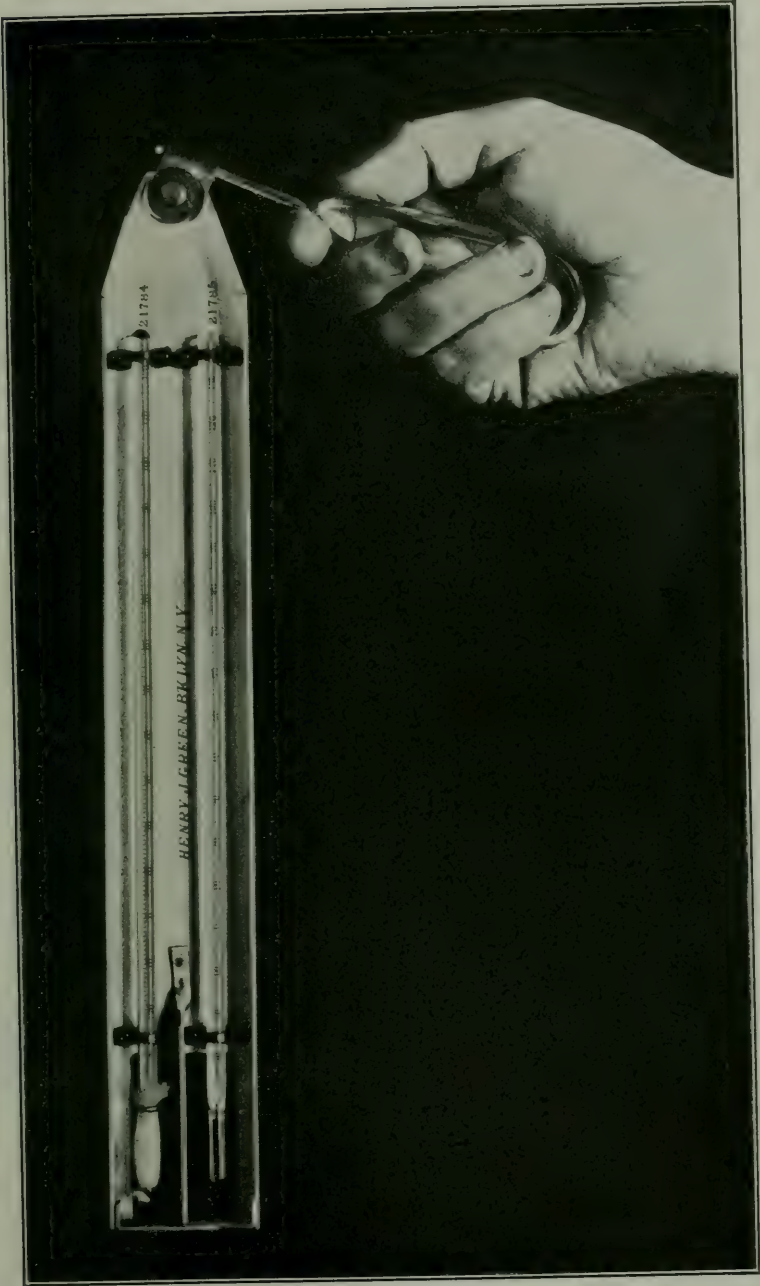
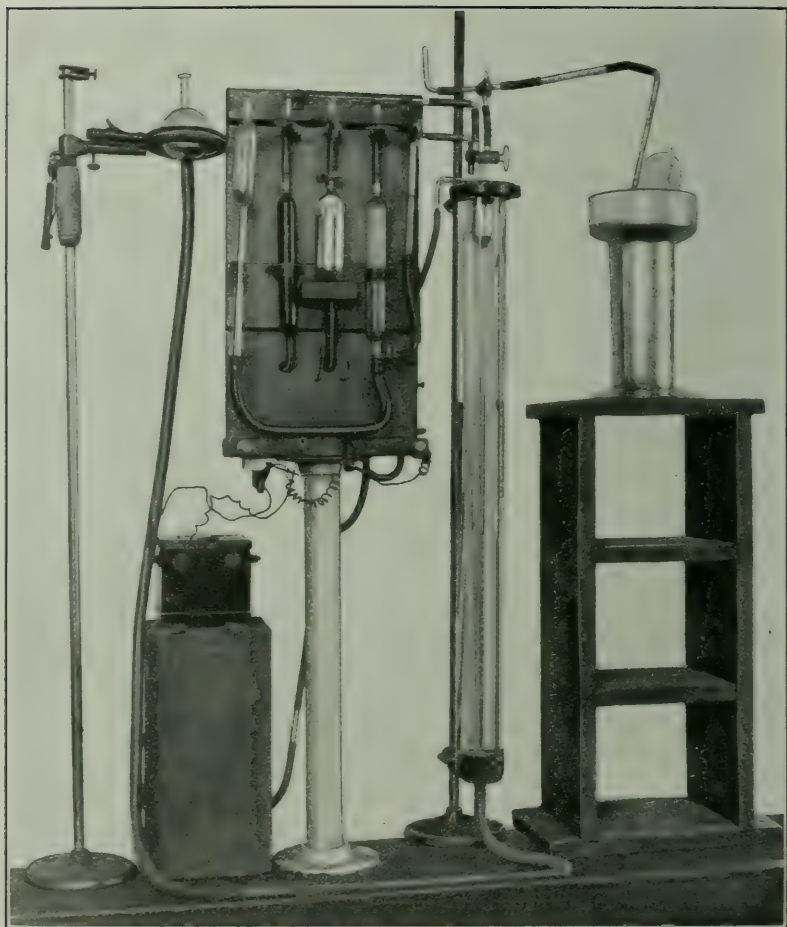


FIGURE 3.—Curves of equal relative humidity for varying temperatures and depressions of wet bulb

100,000 cubic feet of air at different temperatures and different degrees of saturation when the barometric pressure is 30 inches of mercury.



SLING PSYCHROMETER



LABORATORY FORM OF APPARATUS FOR THE EXACT ANALYSIS OF MINE AIR

Exact results can be obtained from these figures when the barometric pressure at the time the wet and dry bulb readings are made

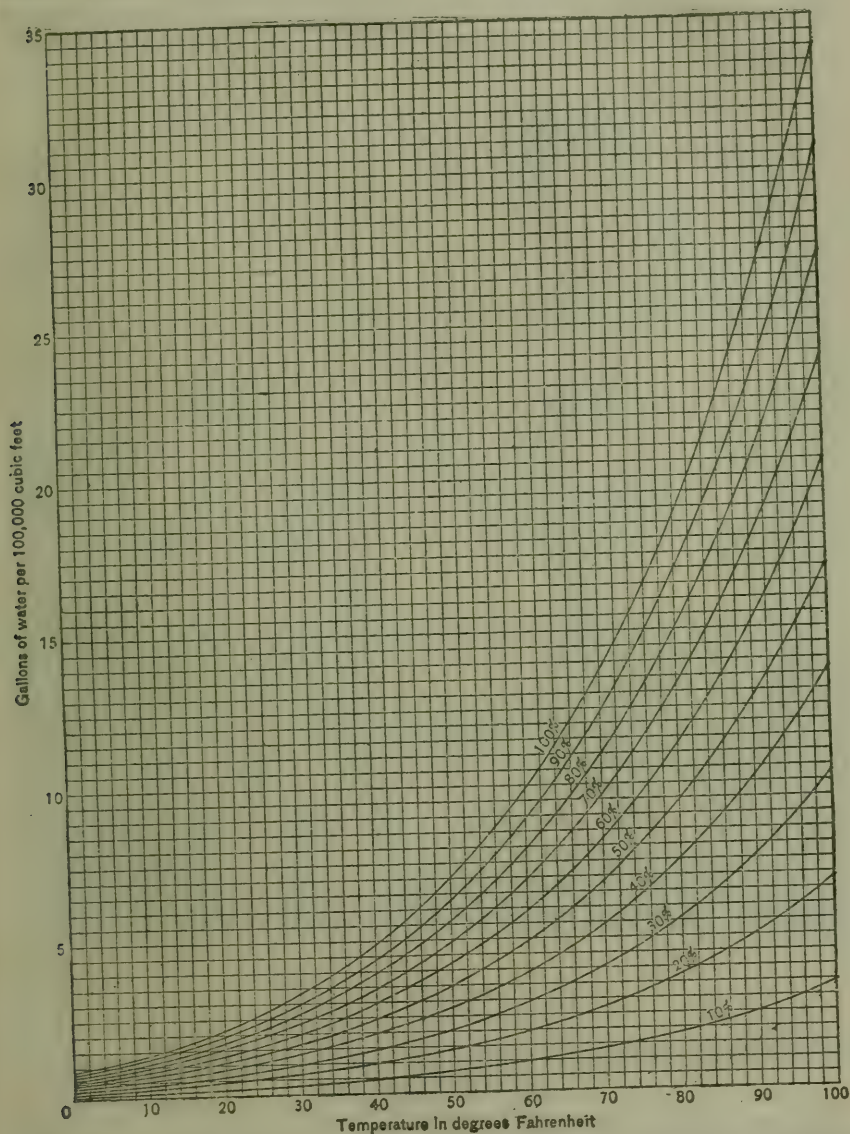


FIGURE 4.—Curves of equal relative humidity for varying temperatures and volumes of water carried

equals 30 inches of mercury. For practical purposes in determining the moisture content of the air of a mine, however, these curves may be used even when the true barometric pressure is much more

or less than 30 inches of mercury. That the barometric pressure may often be neglected is shown by the tabulation below of the relative humidity of atmospheres when the wet-bulb reading is 67° F. and the dry-bulb reading is 75° F., at different barometric pressures:

Relative humidity with different barometric pressures

Barometric pressure, inches of mercury :	Per cent
25-----	68
27-----	67
29-----	66
30-----	66

Results of gas analysis, as determined in the laboratory and reported, are on the dry or moisture-free basis; all air, however, contains a certain proportion of moisture. This quantity can be determined and included in the analyses, but the percentage of each of the other constituents will, of course, be lowered thereby. If the sample contains 2 per cent of moisture, a not uncommon proportion, and the oxygen as determined by analysis is 20 per cent, the true percentage of oxygen, when allowance is made for the water vapor, becomes 19.60 per cent. The proportions of oxygen and nitrogen are affected most.

Tables have been carefully worked out to show the pressure of aqueous vapor at saturation for different temperatures. Hence, if the degree of saturation of the air with aqueous vapor is obtained by means of the sling psychrometer, the aqueous tension of the water vapor present in the air can be determined and the percentage by volume of the aqueous vapor found from the ratio of the partial pressure of the water vapor to the total barometric pressure. Thus, if the air is 41 per cent saturated at 20.6° C., the pressure of the aqueous vapor is 7.86 mm. of mercury. If the total barometric pressure is 746 mm. of mercury, the percentage of aqueous vapor by volume is

$$\frac{7.86}{746} \times 100 = 1.05 \text{ per cent}$$

LABORATORY APPARATUS FOR THE DETERMINATION OF MOISTURE IN MINE AIR

Figure 5 shows an apparatus assembled by the authors for the determination of moisture in gas samples. It works on the same principle as Pettersson's apparatus, as described by Hempel,¹⁰ except that the gas sample is passed over phosphorus pentoxide instead of being confined in a tube containing the phosphorus pentoxide under pressure until the dehydrating action is complete. Hempel

¹⁰ Hempel, Walther, Methods of gas analysis. 3d German ed., trans. by L. M. Dennis, 1910, p. 346.

has shown that Pettersson's method is slow, and that at least 20 minutes must be allowed for the complete removal of the moisture from the air. When the apparatus shown in Figure 5 was used, however, two or three fairly rapid passages of the sample over the phosphorus pentoxide sufficed for the complete removal of the moisture.

The apparatus shown in Figure 5 consists essentially of the burette *a*, the phosphorus pentoxide tube *b*, the water jacket *g*, and the mercury reservoir *h*. To make a determination draw the gas sample into the burette through the three-way stopcock *e*, and measure it against the air in the compensating tube *c* by bringing the mercury in the manometer tube *d* to the mark *f*. Then pass the sample slowly through the phosphorus pentoxide tube *b* into the mercury reservoir *h*. Three or four passages of the gas sample back and forth between the burette and the mercury reservoir are enough. Measure the gas sample again as at first beginning, and record the loss in volume as moisture.

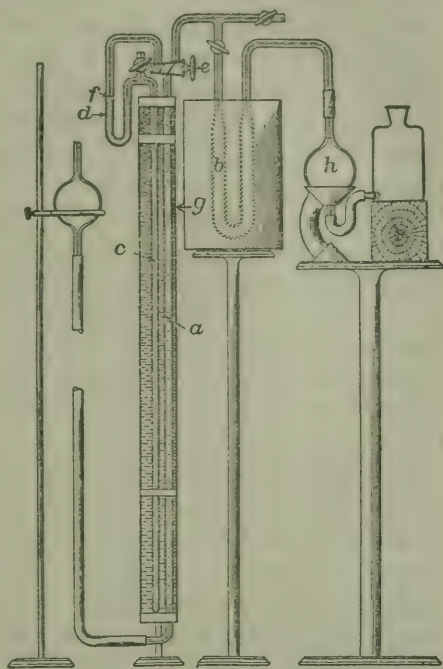


FIGURE 5.—Apparatus for determination of moisture in gas mixture. For explanation, see text

The following series of results compare the percentages of water vapor in the laboratory air as determined by means of the sling psychrometer and by absorption with phosphorus pentoxide. The thermometers were graduated to 0.1°.

Determination of water vapor in air

Psychrometer method	Phosphorus pentoxide method
<i>Per cent</i>	<i>Per cent</i>
0.88	0.77
1.02	.94
1.22	1.14
1.02	1.07
.97	.84
1.02	.88
1.10	.90

ANALYSIS OF MINE ATMOSPHERES

REASONS FOR USING PRECISE METHODS

Some of the constituents in mine air are present in extremely small proportions, less than 0.1 per cent of methane, for example, and an equally low content of carbon dioxide. If any methane is present, the management of a mine will want to know it, because any derangement of the ventilating system may allow large quantities of the gas to accumulate. Such accumulations have caused disastrous explosions. Small percentages of methane in the return air current may represent a large volume, measured in terms of cubic feet, expelled in 24 hours. If a current of 100,000 cubic feet of air per minute contains only 0.1 per cent of methane, it discharges 144,000 cubic feet of this gas every 24 hours. A current of the same volume carrying 0.5 per cent of methane, a proportion that is not by any means unknown, discharges 720,000 cubic feet of methane in 24 hours.

Carbon monoxide, which is produced in mines by fires and explosions, is harmful even in very small proportions,¹¹ and any information as to the amount produced is important.

In addition, certain questions, some a matter of dispute among mining men, can be answered only by a close study of mine air. One of these is whether traces of carbon monoxide, and olefin hydrocarbons, hydrogen, or paraffin hydrocarbons other than methane may be found in normal mine air,¹² and whether they are given off from the pores of the coal and the cracks in a coal bed, or whether under some conditions they are formed by the action of the oxygen of the air on the coal at normal temperatures.

A study of the effect of barometric pressure on the escape of methane in coal mines demands that analyses be performed with especial precision, in order that small changes in the composition of the mine air may be detected. After explosives have been fired in mines, the air may contain certain explosive and noxious gases in extremely small proportions, and because some of these gases are very harmful, even in such proportions, apparatus with which exact work can be done must be used.

OLDER TYPES OF APPARATUS

Winkler's¹³ titration apparatus for the examination of mine air for methane is greatly favored by some mining companies. In connection with Winkler's apparatus, Hesse's¹⁴ apparatus for de-

¹¹ Sayers, R. R., and Yant, W. P., Dangers of and treatment for carbon monoxide: Repts. of Investigations, Serial No. 2476, Bureau of Mines, May, 1923.

¹² By "normal mine air" the authors mean the air in a mine that is operating under normal conditions.

¹³ Winkler, Clemens, Handbook of technical gas analysis. 2d English ed., trans. from 3d German ed. by George Lunge, 1902, p. 156.

¹⁴ Winkler, Clemens. Work cited, p. 103.

termination of carbon dioxide is used. Both apparatus provide for the absorption of carbon dioxide by a standard solution of barium hydrate and the subsequent titration of the excess of barium hydrate with a standard solution of oxalic acid.

The method is accurate, the necessary apparatus inexpensive, and their parts easily replaced when broken. A sample measuring at least 200 or 300 c. c. should be taken for analysis. With still larger samples more accurate work can be done. Carbon dioxide and methane only can be determined with this equipment. When the methane is present in proportions at or above the lower explosive limit of mixtures of methane and air (about 5 per cent methane), some other method must be adopted. By Winkler's method the carbon dioxide produced by the combustion is assumed to represent the methane originally present in the mine air. This assumption is undoubtedly true for most mine atmospheres, but does not hold for some samples representing conditions other than normal.

The types of apparatus designed by Hempel, Elliot, Orsat, and others for the analysis of producer gas, illuminating gas, or flue gas are scarcely accurate enough for use in examining mine gases. In the hands of a skilled gas analyst Haldane's¹⁵ apparatus gives excellent results. Carbon dioxide, oxygen, carbon monoxide, hydrogen, and methane can be determined with an accuracy of about 0.01 to 0.02 per cent. The determination of methane alone necessitates only the transfer of the sample to the burette, its measurement therein, its combustion, and the final measurements of the contraction in volume produced by the combustion. The determination can be accomplished in about 10 minutes. The instrument must be given the care accorded any correspondingly accurate eudiometric apparatus. It should be protected from drafts, the mercury and the burette should be kept clean, and the solutions should be brought exactly to their respective marks before the burette is read.

MODIFIED HALDANE APPARATUS

APPLICATION AND USE

The Haldane apparatus (see Pls. II, p. 9, and III, p. 18) used by the Bureau of Mines for the analysis of mine air and similar gases is patterned after the original device used by Haldane, and differs only in minor features which have been introduced to simplify its construction and make it easier to operate.

The apparatus is especially adapted for the analysis of gases containing small quantities of combustibles, carbon dioxide, and varying amounts of oxygen. The percentage of combustibles present must be below the explosive limit, and enough oxygen must be pres-

¹⁵ Foster, C. LeN., and Haldane, J. S., *The investigation of mine air*. 1905, p. 101.

ent in the gas itself to burn the combustibles completely. From the contraction in volume, the carbon dioxide produced, and the oxygen consumed when the combustibles are burned, the kind and quantity of the combustible gases present can be determined. However, with this apparatus only three combustibles can be determined, and under certain conditions only two.

The Haldane apparatus is useful for the analysis of gases in which the constituents are present in amounts too small for accurate determination by the usual methods—that is, less than 0.1 or 0.2 per cent. It is accurate enough for determining constituents in amounts of 0.02 per cent or more but can not be used for accurate determinations below 0.02 per cent; for proportions as small as this special methods using large quantities of the gas must be employed. The construction of the burette requires that at least 75 per cent of the sample must consist of an inert gas, such as nitrogen, or a constituent which is not analyzed. These restrictions limit the application of the apparatus to certain types of analysis.

The Haldane apparatus is especially suitable for the analysis of mine gases containing small quantities of combustibles and atmospheres to which workmen are continually exposed. The Bureau of Mines uses this apparatus almost exclusively for studying the many ventilation problems pertaining to coal and metal mines. It can also be used for the accurate analysis of flue gases, synthetic mixtures of carbon dioxide, natural gas, gasoline vapors, benzene, carbon monoxide, hydrogen, methane, and air below the explosive limit; and to determine small amounts of hydrogen or oxygen in mixtures of the two gases.

FACTORS AFFECTING THE ACCURACY OF ANALYSIS

The following factors must be considered and eliminated, or corrections must be made for them, to insure accurate analysis of a gas.

1. Change of temperature and pressure during the analysis.
2. Change of water-vapor content.
3. Solubility of the gases in the confining liquid.
4. Solubility of the gases by the absorbent.
5. Graduation of the burette.

CHANGE OF TEMPERATURE AND PRESSURE DURING THE ANALYSIS

When the temperature of a volume of gas is increased 1° F., the gas expands approximately one four hundred and ninety-second of its initial volume at 32° F., if the pressure does not change. In other words, a change of 5° F. during an analysis makes a difference of about 1 per cent in the volume. Since gas analysis is in reality a series of observations of changes of volume when the gas is treated

by different absorbents or subjected to various processes, a temperature change may indicate certain constituents when none are present. For example, assume that during the analysis for carbon dioxide the temperature falls 5° F.; here an apparatus not compensated for changes of temperature would indicate about 1 per cent too much carbon dioxide in the gas. Likewise, a change of 1 mm. pressure of mercury will change the volume of a gas by one seven hundred and sixtieth of its initial volume at sea level and constant temperature. It is therefore very important to apply corrections for change of temperature and pressure when each volume reading is recorded, or to use a compensating device which corrects for these changes.

The Haldane apparatus compensates for change of temperature and pressure (barometric changes) by an auxiliary tube inclosed in the water jacket with the burette, so that any such changes during an analysis affect the gas in the burette and the compensating tube to the same extent. This device, which eliminates the effect of change of temperature and pressure during the analysis, is more fully discussed in the text explaining the operation of the apparatus.

CHANGE OF WATER-VAPOR CONTENT

The variations of gas volume due to change of water-vapor content, temperature, and pressure are given by the following formula:

$$V_1 = \frac{V_2 (P_2 - W_2) (273 + T_1)}{(P_1 - W_1) (273 + T_2)}$$

where V_2 = observed volume of gas at the observed temperature T_2 .

V_1 = calculated volume of gas at the temperature T_1 .

P_2 and P_1 = respective barometer pressure in millimeters of mercury.

T_2 and T_1 = respective temperatures in degrees Centigrade.

W_2 and W_1 = respective vapor tension of water vapor in millimeters of mercury.

A rise of temperature increases the tension of water vapor, therefore, unless certain precautions are taken, the compensating device described will not compensate for change in the vapor tension of water vapor in a gas. To accomplish this, always keep a film of water in the burette over the mercury, so that any gas drawn into the burette becomes saturated with water vapor. Likewise, keep 1 or 2 c. c. of water in the compensator tube so that the air in this tube is saturated. When the temperature of the gas in the burette increases, and the vapor tension becomes proportionately greater, the vapor tension of the gas in the compensator tube increases to the same extent and corrects for this error.

SOLUBILITY OF GAS IN CONFINING LIQUIDS

All gases, especially carbon dioxide, some of the unsaturated hydrocarbons, and gases of high molecular weight, are soluble to some extent in water. To eliminate this error of solubility, mercury is used as the confining liquid in the burette and combustion pipette, and for trapping the gas samples during the analysis.

SOLUBILITY OF GASES BY ABSORBENTS

In gas analysis the constituents are either removed by solid or liquid absorbents, which take out certain constituents and leave the remainder; or, if they are combustibles, they are determined by certain combustion relations resulting from the burning of the combustibles with oxygen to carbon dioxide and water. The range of precision of an analysis is limited by the absorbents available for removing the different constituents. Not only do the absorbents remove some constituents chemically, but certain other constituents dissolve physically in the absorbent. The physical solubility of the gases usually analyzed with the Haldane apparatus is not great—oxygen, nitrogen, methane, carbon monoxide, and hydrogen are but slightly soluble in a solution of potassium hydroxide, and after one or two analyses have been made the solubility error becomes inappreciable. In a solution of alkaline pyrogallate, however, the solubility of the four last gases is somewhat larger. Whenever a fresh solution of caustic pyrogallate is put in the apparatus, at least two analyses should be made before the oxygen percentage is taken as the true result, because a fresh solution of alkaline pyrogallate absorbs some nitrogen gas as well as oxygen, and abnormally high results are obtained for the first one or two analyses.

GRADUATION OF THE BURETTE

Accurate results can not be obtained unless the burette is properly calibrated. Makers of burettes usually calibrate them with fair accuracy, but accurate calibration of the entire length of the bore is difficult if the burette is narrow and graduated into hundredths of a cubic centimeter; consequently a check calibration should be made as follows: Leave the burette in the water jacket in the same position as used, and keep the temperature of the water as constant as possible. Seal a three-way stopcock to the lower end of the burette, and attach a leveling bottle to one projection of the stopcock, so that if by accident the mercury is allowed to fall below a certain graduation mark on the burette during the calibration the bottle can be raised and the mercury conveniently brought back to the mark for the calibration. Weigh successive 1-c. c. portions of mercury, and calculate the volume of the mercury at the observed

temperature from the weight. Plate III shows a diagrammatic section of the apparatus.

DESCRIPTION OF APPARATUS

The burette has a total capacity of 21 c. c. The bulb at the upper part has a capacity of 15 c. c., and is not graduated. The stem has a capacity of 6 c. c., and is graduated in hundredths of a cubic centimeter. The burette is graduated from the bottom of stopcock *g*, at the point where the sample is drawn into it.

BURETTE AND PIPETTES

The burette is connected to pipettes *m*, *l*, and *n* by a capillary glass manifold, as shown. Pipette *n* contains caustic potash for removing carbon dioxide; pipette *l* has a platinum spiral, which, when heated bright yellow, burns the combustibles to carbon dioxide and water; and pipette *m* contains alkaline pyrogallate solution for removing the oxygen. Pipettes *m* and *l* are connected with storage bulbs *w* and *x* on the back of the apparatus by heavy-walled rubber tubing.

A compensator tube is provided in the water jacket *z* surrounding the burette; it connects by way of the three-way cock *f* and capillary tubing to pipette *n*, as shown.

TRANSFER OF SAMPLES

One branch of the three-way parallel cock *g* at the top of the burette connects to three-way cock *h*, and thence by capillary tubing to the gooseneck *j*, and the sample of gas to be analyzed. The figure shows the method by which the gas is removed from a vacuum bottle, the receptacle recommended by the Bureau of Mines for sampling gases. The neck of the gas sample-bottle is broken off under mercury in the bell jar *i*, and the gooseneck *j* inserted. In this manner gas can leave the sample only through the capillary connected to cock *h*; likewise air can not enter and contaminate the sample. As the gas is withdrawn, mercury rises from the bell jar and fills the space occupied by the gas. If this method of sampling is not used, the gooseneck is removed and the sample bottle is connected direct to the right branch of stopcock *h*.

ELECTRIC CONNECTIONS

The sketch shows a small transformer which is connected to the source of energy. At the gas laboratory of the Pittsburgh experiment station of the Bureau of Mines the transformer receives alternating current at 110 volts, which is reduced to 6 volts and connected to the apparatus. The transformer has a variable range of

11½ to 30 volts, so that different sizes and lengths of wires may be used. One of the leads b from the transformer connects with switch k , then to a sliding connection, u , which can be moved along a 22-gauge nichrome resistance wire as shown. From one of the binding posts the lead connects directly to the combustion pipette, as shown in the detail drawing, Plate IV (p. 24). A loop of heavy platinum wire (No. 22, Brown & Sharpe gauge) is sealed in the bottom of each glass electrode to which the leads connect. The glass electrodes are filled with mercury and serve as the circuit to the platinum spiral at the top. The electrodes are open at the top, so that they can be filled with mercury, and the ends of the 2½-inch platinum spiral of No. 30 Brown & Sharpe gauge wire are fastened in the tops of the electrodes by small glass buttons. Thus the spiral is kept in the proper position at all times and makes good contact with the mercury.

The other lead (b^1) from the transformer, connects directly to one of the glass electrodes on the pipette.

The nichrome wire allows more careful regulation of the temperature of the platinum spiral than can be obtained by the transformer. A gas containing an unduly large amount of combustibles causes the wire to become very hot, and unless some additional resistance is added the wire may be burned out. By sliding the contact along the nichrome wire the operator keeps the temperature of the wire completely under control at all times.

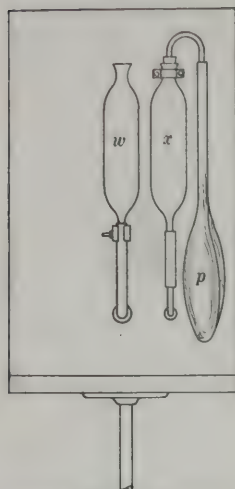
If a transformer is not available a storage battery that will produce an electric current of 4 amperes at 5 volts may be used to heat the platinum wire to incandescence. Dry cells may be used in emergency, but they are not as satisfactory as a storage battery, since long-continued use runs them down.

An electric light bank may be used if a suitable number of carbon electric lights is connected in parallel, and the platinum spiral connected in series with the electric lighting circuit.

OTHER PARTS OF APPARATUS

A rubber bag is attached to the rear branch of the pyrogallate pipette to keep the solution from coming in contact with the air, otherwise the solution would soon be exhausted by the absorption of atmospheric oxygen. If a rubber bag is not used the pyrogallate solution may be covered with a layer of mineral oil to exclude the outside oxygen.

Plate III shows a device, γ , for raising and lowering the mercury leveling bulb r ; it is convenient for bringing the solutions to the marks. An ordinary ring support with a screw clamp may be used as easily.



REAR VIEW OF BOARD

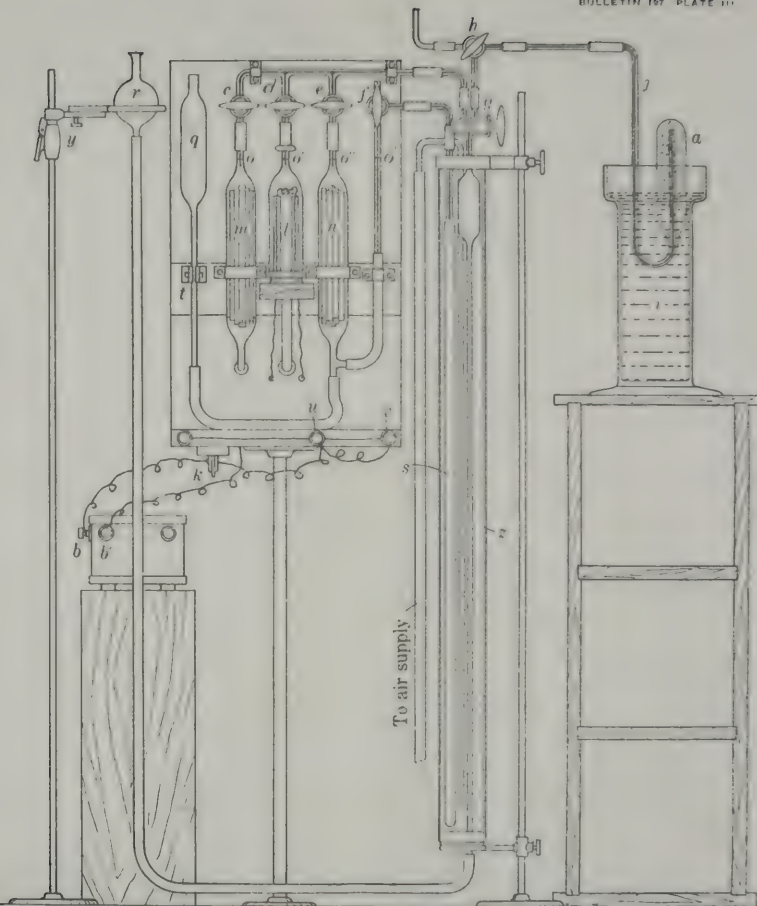


DIAGRAM OF LABORATORY FORM OF APPARATUS FOR EXACT ANALYSIS OF MINE AIR



LEAF AND SEED

PREPARING THE APPARATUS FOR USE

Fill the burette and leveling bulb *r* with pure distilled mercury until, when *r* is raised and the mercury rises to the cock *g*, 2 or 3 c. c. of mercury remains in *r*. Additional mercury is unnecessary, and only adds to the weight to be raised and lowered during the analysis.

Put 1 or 2 c. c. of distilled water, for reasons already given, into the compensation tube before it is assembled in the water-jacket.

Pour caustic solution into the storage bulb *q* until, with cocks *e* and *f* removed, the solution comes to the mark *o''* on pipette *n*; then replace cocks *e* and *f*. Remove the glass electrodes in combustion pipette *l* and fill them with mercury, using a capillary funnel to introduce the mercury therein and taking care that no air bubbles are present, otherwise the electrodes will not conduct the electric current. Next replace the electrodes in the pipette, and force securely into the bottom of the pipette the rubber stopper holding them. The mercury exerts a great pressure on the rubber stopper and some may leak out unless the stopper is tight. Pour mercury into the storage bulb *w* until when cock *d* is removed the level just comes to the mark *o'* in pipette *l*; cock *d* is then replaced.

Pour caustic pyrogallate into storage bulb *x* until, with cock *c* removed, the level of the solution just comes to mark *o*. Replace cock *c*, slightly inflate rubber bag *p*, and connect it to *x* by a rubber stopper and a U-shaped glass tube, as shown. Caustic pyrogallate solution is viscous and disagreeable to handle and should not be exposed to the air longer than necessary. A satisfactory method of preparing the solution is to use 350-c. c. magnesium citrate bottles; from these it can easily be poured directly into the pipette with minimum contact with the air.

GREASING THE STOPCOCKS

Lubricate all stopcocks carefully with a good grease. Vaseline alone is not satisfactory for the Haldane apparatus, but should be incorporated with pure gum rubber and beeswax, as described later. Wipe the cocks thoroughly with cheesecloth to remove old grease and clean the capillary bores by passing a small copper wire through them. Pipe cleaners are better than copper wire. To clean the barrel of the cock most satisfactorily wrap one or two thicknesses of cheesecloth over the end of a lead pencil and pass them through the barrel, at the same time giving the pencil a rotary motion. Then clean the capillary leading to the cock with a pipe cleaner or copper wire. Rub a small amount of the grease over the plug of the cock and distribute it evenly over the entire length. Remove the grease that gets into the bore. Replace the plug in the barrel and give it a rotary motion in both directions, exerting pressure at the same

time. If the cock is properly greased there should be an even, transparent film throughout its entire length. Should any striations or bubbles show, especially at the neck of the plug, remove the cock and regrease it.

These instructions on the greasing of stopcocks have been given because proper greasing is very important and essential to the accurate analysis of gases. The usual tendency is to use too much grease, and after the cock is turned a few times the bore and capillaries become filled with grease; endless trouble follows and the solutions often rise into the manifold.

Draw one or two drops of water into the burette by turning cock *g* to communicate with *h*, and by turning *h* to communicate with the outside air. Raise bulb *r* until mercury flows out of the left branch of cock *h*; then dip the capillary tube connected to *h* and bend at right angles into a beaker containing water, draw a few cubic centimeters into the burette, lower *r* until the level of the mercury in the burette is near the bottom, and elevate *r* until mercury again flows out of the connection at *h*. Enough water sticks to the sides of the burette by this procedure to saturate the gases to be analyzed, and so prevents an excess of water in the burette, which would give erroneous gas-volume readings.

The solutions in the pipettes are now brought to their respective marks by the following procedure: Take 19.5 to 20 c. c. of gas into the burette by way of cocks *g* and *h*; then turn *g* 180°, connecting the burette with the manifold; open cock *e* and raise or lower leveling bulb *r*, as the case may be, until the level of the solution comes to mark *o''*. In a similar manner bring the levels in pipettes *l* and *m* to the marks *o'* and *o''*.

TESTING FOR TIGHTNESS

The analyst should now test the apparatus for leaks, remembering that even a very small leak will make the results obtained in the Harkness apparatus practically valueless, especially when three combustibles are present. Large leaks are easily found and removed, but small leaks are difficult to detect.

To test for leaks proceed systematically by first drawing into the burette about 20 c. c. of air and closing cock *g*. Then raise leveling bulb *r*, and put the gas in the burette under pressure; raise *r* until the mercury level is just below the bulb part of the burette, and hold it in this position. Observe whether the mercury level rises in the burette. A gradual rise indicates a leak in cock *g*. If the mercury level remains stationary, turn cock *g* to connect with the manifold, which places it under pressure, and test cocks *c*, *d*, and *e* for leaks. A leak in any of these usually, although not always, causes the solutions to drop from the marks *o*, *o'* and *o''*. If the

solutions do not drop and the mercury level in the burette does not rise, the cocks *c*, *d*, and *e* are gas-tight. Next make tests for leaks at the rubber connections below the cocks *c*, *d*, and *e*. Test pipettes *m* and *l* by removing storage reservoirs *x* and *w* on the back of the apparatus and lowering them several inches with cocks *c* and *d* closed. When *x* and *w* are replaced on the supports the liquids should come back to the marks *o* and *o'*.

If there are no leaks in the manifold, test the compensator and pipette *n*. With cock *f* open to the air, raise leveling bulb *q* until the level of the caustic solution nearly reaches cock *f*, then turn *f* 90° to the right, making connection with the compensator tube *s*. Lower *q* as far as possible by removing it from the clamp, noting whether the liquid in the small tube below cock *f* falls. If the liquid falls, there is a leak in the compensatory tube, and all the rubber connections should be examined and made gas-tight. Also, if the solution in *n* falls when the compensator is tested there is a leak in *n*.

Lastly, test the tightness of the capillary line connecting the sample tube with the burette by raising leveling bulb *r* until the mercury in the burette reaches cock *g*, placing a finger over the open end of the gooseneck, lowering leveling bulb *r*, and observing the mercury level to see whether it falls. Should the mercury level continue to fall, there is a leak in the line somewhere between the gooseneck and cock *g*.

The above tests should detect any leaks. Each time the apparatus is used, provided it has been idle several days, all connections and cocks should be examined as outlined.

Heavy rubber bands are very satisfactory for making gas-tight connections between the rubber tubing and the glass. Stretch and wrap a piece of rubber band about 2 inches long around the connection several times and tuck the free end under the last winding, drawing it up tight, as in tying with string. It is difficult to wrap some parts of the apparatus with rubber bands. In such places use No. 20 copper wire, winding the wire twice around the connection, and then drawing it up tight by twisting the free ends with pliers.

PREPARATION OF SOLUTIONS

CAUSTIC POTASH SOLUTION

For the removal of carbon dioxide, use caustic potash or soda solution. Prepare the potash solution in the proportions of 30 grams of stick potassium hydroxide in 100 c. c. of water.

CAUSTIC SODA SOLUTION

Caustic soda is equally good for removing carbon dioxide. Long use causes the precipitation of a white deposit of bicarbonate on

the glass tubes, but this is easily removed by washing the pipette with dilute hydrochloric acid before it is refilled with fresh solution. Prepare the caustic soda solution in the proportion of 20 grams of stick sodium hydroxide to 100 c. c. of water.

ALKALINE PYROGALLATE SOLUTION

Alkaline pyrogallate solution requires a high concentration of alkali to prevent the production of carbon monoxide when the solution reacts with the oxygen. Moreover, the proportions of pyrogallic acid must not be too great, otherwise the solution becomes too dark for easy readings. Solutions filling the above requirements are prepared as follows:

1. POTASSIUM PYROGALLATE SOLUTION

Dissolve 1,200 grams of stick potassium hydroxide in 800 c. c. of water, and in another receptacle dissolve 50 grams of pyrogallic acid in 150 c. c. of water.

When the potassium hydroxide is cool distribute it evenly in four 350-c. c. magnesium citrate bottles; add the pyrogallic acid solution, 46 c. c. to each bottle. Stopper the bottles tightly by the spring clamps provided and shake them to mix the solutions, which are then ready for use. If the reagent is prepared in the bottles as described, it may be kept indefinitely without deterioration.

2. SODIUM PYROGALLATE SOLUTION

A solution that gives off a minimum amount of carbon monoxide, has a fairly high rate of absorption, and is adapted for pipettes using glass tubes¹⁶ is prepared as follows: Dissolve stick sodium hydroxide in an equal weight of water; this constitutes the stock sodium hydroxide solution. In another receptacle make up stock pyrogallic acid solution in proportions of 1 gram of pyrogallic acid to 3 c. c. of water. If the mixture is to be kept in 350-c. c. magnesium citrate bottles, place 250 c. c. of the sodium hydroxide in each bottle and add 100 c. c. of the pyrogallic acid solution. Stopper the bottles quickly and shake to mix the solutions, which are then ready for use.

PROCEDURE FOR ANALYSIS

Before a sample of gas is taken into the apparatus adjust the compensator by turning cock *f* to the air and raising or lowering *g* until the level of the caustic solution comes to the mark *o'''* on the capillary tube below *f*. Then close *f*, making connection with the compensator tube *s*, and leave it closed during the entire analysis.

¹⁶ Jones, G. W., and Meighan, M. H., Sodium pyrogallate solution as an absorbent for oxygen: Jour. Ind. Eng. Chem., vol. 11, 1919, p. 311.

If the gas to be analyzed is contained in a vacuum sample bottle as shown in Figure 1 (p. 3), make a file mark part way around the neck, place the end under mercury in the jar *i*, and break the neck off by tapping it against the side of the jar. Then introduce gooseneck *j* into the sample tube as shown. If the gas is contained in a sample tube of the type having connections on either end, remove the gooseneck and connect the sample at this point, dipping the other end into the bell jar *i*.

TAKING GAS INTO APPARATUS

To begin the analysis, turn cock *g* to connect with *h* and the outside air; raise leveling bulb *r* until mercury flows out of the left capillary connecting with *h*; then turn cock *h* 90° to the left, making connection with the sample of gas; lower leveling bulb *r*, drawing in a sample of gas. When the mercury level reaches the 20-c. c. mark, again turn cock *h* 90° to the right and raise *r*, forcing the gas out of the burette. Discard this sample because it is contaminated with air in the capillary between the gooseneck and cock *h*. When the mercury reaches cock *h* again turn *h* 90° to the left, making connection with the sample; lower leveling bulb *r*, drawing in a sample of gas. When approximately 20 c. c. has been drawn into the burette, as indicated by the mercury level, turn cock *g* 180°, connecting the burette with the manifold. Raise leveling bulb *r* about 1 inch to prevent the caustic solution from rising and getting into the manifold when cock *e* is opened. Open cock *e*, and raise or lower *r* until the caustic solution comes to the mark *o''*. At the same time, raise or lower leveling bulb *q* until the caustic solution comes to the mark *o'''* on the compensator. When the solutions are on both marks, read the volume of gas in the burette to the nearest 0.002 c. c. This reading gives the volume of sample taken for analysis.

TEST FOR CARBON DIOXIDE

Remove the carbon dioxide by raising and lowering leveling bulb *r*, thus forcing the gas back and forth into the caustic pipette *n*. When the gas has been passed six times into the caustic pipette, read its volume again by compensating in the manner described before. Check this reading by passing the gas six times more and noting whether there is any further contraction. When this volume is subtracted from the volume of sample taken, the result gives the contraction due to carbon dioxide, and when divided by the volume of the sample taken for analysis and multiplied by 100 the result is the percentage of carbon dioxide in the sample.

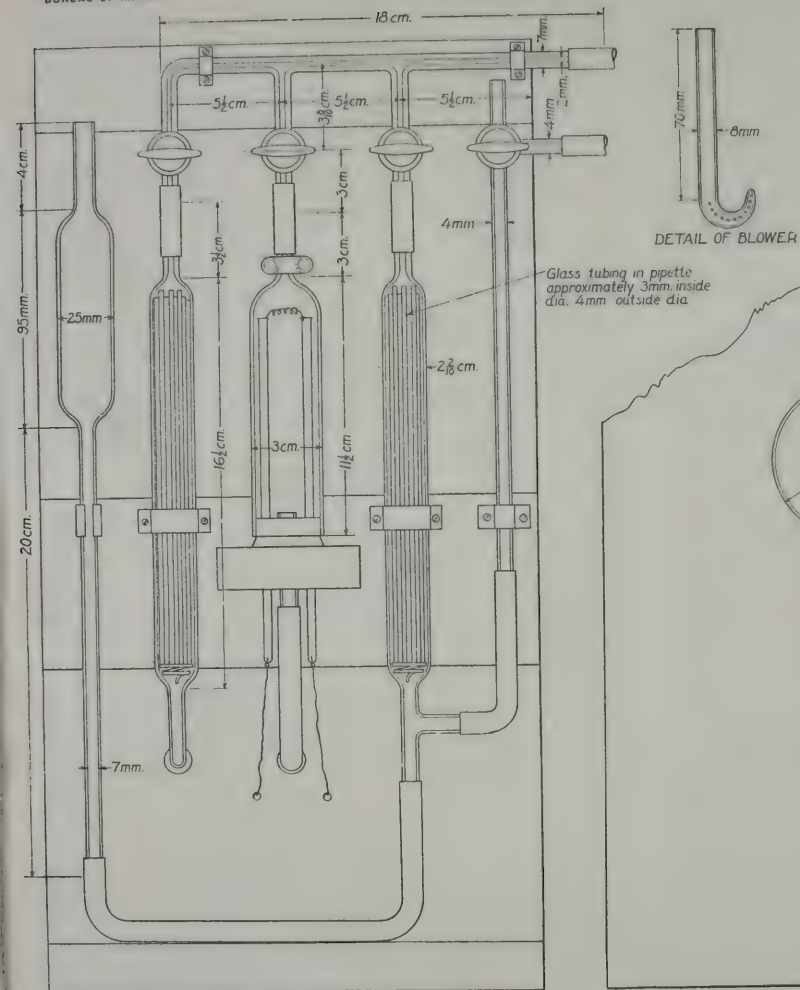
Next, determine the combustibles by passing the gas into pipette *l* by closing cock *e*, opening cock *d*, and raising leveling bulb *r*. Close

switch *k*, allowing the electric current to pass through the platinum spiral, and adjust the temperature by throwing resistance in or out by sliding contact *u* along the wire on the front of the apparatus. Adjust the temperature of the wire until the wire is bright yellow. If the gas contains appreciable amounts of combustibles, add more resistance by sliding *u* to the left, otherwise the platinum spiral may be burned out. Pass the gas back and forth over the platinum spiral by raising and lowering *r* at least twelve times. Keep the pipette cold by directing a stream of air over it while the spiral is heated, using a curved glass tube with many small holes in the bottom (see Pl. IV). With a rubber tube the blower may be connected to a compressed-air line, rotary blower, foot bellows, or other suitable source of air.

After the gas has been passed back and forth over the glowing platinum spiral twelve time or more, open switch *k* and cool the pipette. Withdraw the gas into the burette and when the mercury level reaches the mark *o'* close cock *d*. Read the contraction due to burning by opening cock *e* and bringing the level of the caustic solution to *o''* and *o'''* before reading. To find the amount of carbon dioxide produced pass the gas six times or more into the caustic pipette and read the volume. If the contraction produced on burning is greater than 0.200 c. c., pass the gas into the combustion pipette, burn it again, and note the contraction and carbon dioxide produced by the second burning. Add the two contractions and carbon dioxide values.

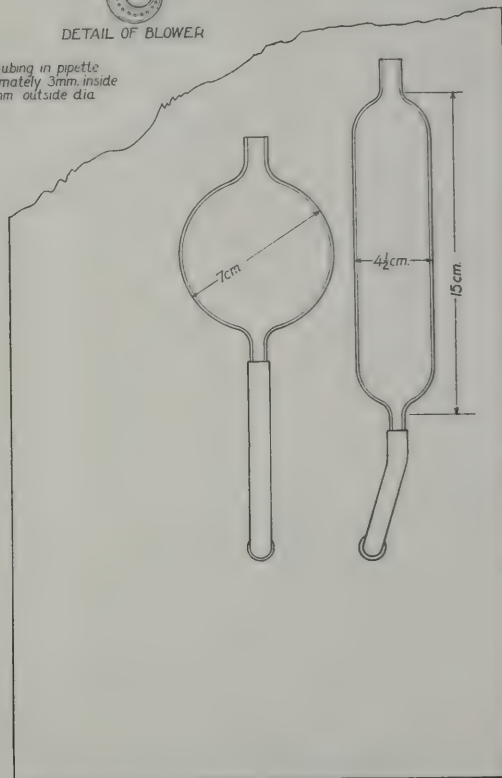
REMOVAL OF OXYGEN

Pass the gas into pipette *m*, which contains alkaline pyrogallate solution; there the oxygen is absorbed. When no further contraction appears to be produced, as indicated by the height of the mercury in the burette when the pyrogallate solution is brought to the mark, remove the oxygen from the capillary tubes connecting the pipettes *l* and *n* before taking a reading. Close cock *c* and pass the gas once or twice into pipette *l*, then a like number of times into pipette *n* to dilute the oxygen in these capillaries. Pass the gas into the pyrogallate pipette again several times, and measure the reduction in volume of gas. Check this value by passing the gas into the pyrogallate pipette again to make sure that the oxygen is completely removed. It must be remembered that the time necessary for removing the oxygen is much longer than for the other constituents, and the contraction due to oxygen should be checked each time before the sample is discarded. Add the oxygen consumed by the combustion of the methane to the oxygen determined by absorption with alkaline pyrogallate solution, if methane is the only combustible gas present.



SIDE VIEW

HALDANE GAS-ANALYSIS APPARATUS



BACK VIEW

Make the different readings in the same manner as described for the original gas volume taken for analysis.

DETERMINATION OF COMBUSTIBLE GAS

The relation between the carbon dioxide and the contraction produced by the combustion indicates the character of the combustible gas present. When the volume of carbon dioxide is just one-half of the contraction, the sample probably contains methane only. The result is confirmed by a second analysis, in which the carbon dioxide is removed and the gas mixture passed directly into the alkaline pyrogallate solution pipette, where the oxygen is absorbed. The difference between the oxygen found by direct determination and that found by the first analysis represents the oxygen consumed in the oxidation of the combustible gases. If methane is the only combustible gas present, the amount of the consumed oxygen should be twice the amount of carbon dioxide formed by combustion. Because methane is the combustible gas usually contained in normal mine atmospheres, a second determination of oxygen is hardly necessary in the analysis of samples of such atmospheres, but the second determination is necessary when from inspection of the combustion data or from the origin of the sample the presence of more than one combustible gas is suspected.

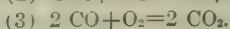
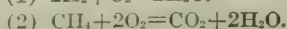
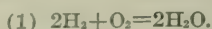
A typical analysis of a sample of gas containing only methane as the combustible constituent follows. The sample was taken from the main return of a coal mine.

Analyses of return air in a coal mine

Stages of analysis:	C. c.
Volume of sample taken-----	20.000
Volume after carbon dioxide absorption-----	19.978
Contraction due to carbon dioxide absorption-----	.022
Volume after combustion-----	19.922
Contraction due to combustion-----	.056
Volume after carbon dioxide absorption-----	19.894
Carbon dioxide due to combustion-----	.028
Volume after alkaline pyrogallate absorption-----	15.820
Partial oxygen-----	4.074
Oxygen consumed in burning methane-----	.056
Total oxygen-----	4.130
Results of analysis:	Per cent
Carbon dioxide-----	0.11
Oxygen-----	20.65
Methane-----	.14
Nitrogen (by difference)-----	79.10
	100.00

CALCULATIONS FOR DETERMINING COMBUSTIBLES

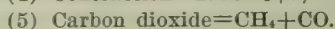
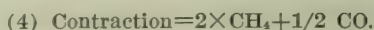
Hydrogen, methane, and carbon monoxide react with oxygen as follows:



When only two of these gases are present in a gas sample, the carbon dioxide and the contraction resulting from burning the gases in the combustion pipette provide enough data for calculating the amount of each combustible gas present.

METHANE AND CARBON MONOXIDE

When only methane and carbon monoxide are present the following relations are obtained from equations (2) and (3):



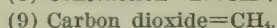
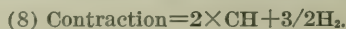
Solving equations (4) and (5)

$$(6) \text{CH}_4 = \frac{2 \times \text{contraction} - \text{CO}_2}{3}$$

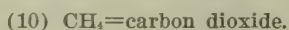
$$(7) \text{CO} = \text{CO}_2 - \text{CH}_4.$$

METHANE AND HYDROGEN

When only methane and hydrogen are present the following relations are obtained from equations (1) and (2):



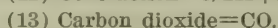
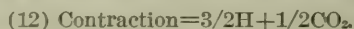
Solving equations (6) and (7):



$$(11) \text{H} = \frac{2 \text{ contraction} - 4 \times \text{CO}_2}{3}.$$

HYDROGEN AND CARBON MONOXIDE

When only hydrogen and carbon monoxide are present the following relations are obtained from equations (1) and (2):



Solving equations (8) and (9):



$$(15) \text{H}_2 = \frac{2 \times \text{contraction} - \text{CO}_2}{3}.$$

HYDROGEN, METHANE, AND CARBON MONOXIDE

When all three gases are present, however, a determination of the amount of oxygen consumed by the combustion of the gases is neces-

sary in order to establish a third known quantity for insertion in the equation, in order to obtain the three equations needed to calculate the quantity of each gas present. The readings in a combustion analysis of a mixture of three gases must be made with precision, because a small error is greatly magnified in the calculations. When these three gases are present the following relations are obtained from equations (1), (2), and (3):

$$(16) \text{ Contraction} = 3/2\text{H}_2 + 2\text{CH}_4 - 1/2\text{CO}.$$

$$(17) \text{ Carbon dioxide} = \text{CH}_4 + \text{CO}.$$

$$(18) \text{ Oxygen consumed} = 1/2\text{H}_2 + 2\text{CH}_4 + 1/2\text{CO}.$$

Solving the above equations:

$$(19) \text{ H}_2 = \text{contraction} - \text{oxygen consumed}.$$

$$(20) \text{ CH}_4 = \frac{2 \text{ contractions} - \text{CO}_2}{3} - \text{H}_2.$$

$$(21) \text{ CO} = \text{CO}_2 - \text{CH}_4.$$

A typical analysis of a gas containing carbon monoxide, hydrogen, and methane follows:

Analysis of mine gas containing CO, H₂, and CH₄

	First sample	C. c.
Volume of sample taken.....	20.430	
Volume after carbon dioxide absorption.....	20.185	
Contraction due to carbon dioxide absorption.....		.245
Volume after combustion.....		20.118
Contraction due to combustion.....		.067
Volume after carbon dioxide absorption.....		20.070
Carbon dioxide due to combustion.....		.048
Volume after alkaline pyrogallate absorption.....		16.280
Residual oxygen.....		3.790
	Second sample	
Volume of sample taken.....	20.270	
Volume after carbon dioxide absorption.....	20.024	
Contraction due to carbon dioxide.....		.246
Volume after alkaline pyrogallate absorption.....		16.204
Contraction due to oxygen absorption.....		3.820

CALCULATION OF RESULTS

From oxygen by second analysis $(3.820 \div 20.270) \times 100 = 18.85$ per cent. If this oxygen value in the first analysis is used for determining the oxygen consumed $(20.430 \times 18.85) \div 100 = 3.851$ c. c. — 3.790 c. c. (residual oxygen) = 0.061 c. c. oxygen consumed during combustion.

By equation (19):

$$\begin{aligned} \text{Hydrogen} &= \text{contraction} - \text{oxygen consumed} \\ &= 0.067 - 0.061 = 0.006 \text{ c. c.} \end{aligned}$$

By equation (20) :

$$\begin{aligned}\text{Methane} &= \frac{2 \text{ contractions} - \text{CO}_2}{3} - \text{H}_2 \\ &= \frac{0.134 - 0.048}{3} - 0.007 = 0.022 \text{ c. c.}\end{aligned}$$

By equation (21) :

$$\begin{aligned}\text{CO} &= \text{CO}_2 - \text{CH}_2 \\ &= 0.048 - 0.022 = 0.026 \text{ c. c.}\end{aligned}$$

Results of analysis

Constituent:	Per cent
Oxygen = $(3.820 \div 20.270) \times 100$ -----	18.85
Carbon dioxide = $(0.245 \div 20.430) \times 100$ -----	1.20
Hydrogen = $(0.006 \div 20.430) \times 100$ -----	.03
Methane = $(0.022 \div 20.430) \times 100$ -----	.11
Carbon monoxide = $(0.026 \div 20.430) \times 100$ -----	.13
Nitrogen (by difference) -----	79.68
	100.00

RATIO OF BLACK DAMP TO AIR

To estimate the black damp and air in the mixture, the results can be calculated by grouping with the carbon dioxide the nitrogen in excess of that necessary to form atmospheric air with oxygen, as follows:

	Per cent		Per cent
Black damp -----	9.73	{ Carbon dioxide -----	1.18
		{ Nitrogen -----	8.55
Air -----	90.00	{ Carbon dioxide -----	.03
		{ Oxygen -----	18.85
		{ Nitrogen -----	71.12
Carbon monoxide (white damp) -----	.13		
Hydrogen -----	.03		
Methane -----	.11		
	100.00		

PRECAUTIONS IN MANIPULATION OF APPARATUS

MERCURY

Keep the mercury clean by occasionally filtering it through chamois skin and allowing it to drop in a fine stream through dilute nitric acid, passing air through it; or by agitating a mixture of mercury and dilute nitric acid with air.

NECESSITY FOR MOISTURE

Slightly moisten the inside of the burette and compensating tube with water. Accurate work can not be done unless the inclosed air is continuously saturated with moisture.

CAPILLARY MANIFOLD

Do not allow the caustic hydrate or alkaline pyrogallate solution to be drawn into the capillary manifold. If that happens, draw dilute sulphuric acid into the burette, pass it through the manifold to neutralize the caustic, and then wash the manifold again with water. One very small drop of caustic will completely ruin the accuracy of the combustion analysis, and this condition must be carefully avoided if results are to be accurate.

TEMPERATURE OF BURETTE JACKET

Maintain all the water in the jacket surrounding the burette at a uniform temperature. Keep the apparatus in a room of uniform temperature, free from air currents, and stir the jacket water during the analysis by bubbling air through it. If compressed air is not available, use a small rubber syringe bulb by introducing into the jacket a glass tube extending to the bottom of the water jacket, the bulb being attached to the upper end of the tube. The bulb should be provided with a valve, which causes it, when squeezed, to act like a pump, forcing air down through the glass tube and into the water in the jacket.

CHECKING THE APPARATUS

Test the working qualities of the apparatus occasionally by an analysis of atmospheric air. Pure dry air contains 0.03 to 0.04 per cent of carbon dioxide and 20.93 of oxygen, but in large cities these proportions may differ slightly.

EFFECT OF DRAFTS

Protect the apparatus from drafts as far as possible and use it in a room where the temperature change is slight. Although the compensating device corrects for change of temperature and pressure, sudden temperature changes may cause the compensation leveling tube to be raised or lowered beyond the working range during an analysis.

CORRECTIONS FOR WATER VAPOR

The analysis is given on a dry basis and must be corrected for content of water vapor, if this is desired, either by testing the air with some satisfactory type of psychrometer when sampled, or by making a special determination, with special apparatus, for water-vapor content.

CLEANING THE APPARATUS

The burette becomes dirty after several weeks of use, due to finely suspended dusts that are usually present in the samples and to a less extent to some of the constituents combining with the mercury and to particles of stopcock grease finding their way into the burette.

To clear the apparatus remove the rubber tubing connecting the leveling bulb with the bottom of the burette and draw in from the bottom a hot solution of 5 per cent nitric acid, completely filling the burette. To do this most easily put a short length of rubber tubing on one of the upper connections of the burette, connecting an aspirator bulb to it and producing suction. The dilute acid removes the mercury. Remove the organic impurities with hot cleaning solution. Allow the dilute acid to run out, and then wash the burette with distilled water, fill it with hot cleaning solution, and allow to stand over night. Prepare the cleaning solution by saturating concentrated sulphuric acid with potassium bichromate.

ATTENTION TO STOPCOCKS

If any stopcocks are not well ground and leaks continually develop make the cocks fit more tightly by grinding with moistened carborundum powder. To make a suitable stopcock grease, melt 50 parts by weight of pure gum rubber, and as it melts add a melted mixture of 10 parts of vaseline and 25 parts of beeswax. If the resulting grease is too soft add more rubber, and if too sticky add beeswax and vaseline. Use a heavier grease in summer than in the winter. The proportions given above will necessarily vary, depending upon the brands of rubber, beeswax, and vaseline used.

APPARATUS FOR THE DETERMINATION OF METHANE IN MINE AIR

In spite of the fact that the apparatus described above and shown in Plates III and IV has been simplified as much as is consistent with accuracy, its proper manipulation requires more than ordinary experience; consequently it may not be practicable for use around a mine. A mine manager particularly desires an apparatus that will determine methane accurately and quickly so that he can control the methane given off each day in different parts of his mine.

GAS DETECTOR

A safety lamp may be used to detect a proportion of methane likely to become quickly dangerous, as the appearance of a cap¹⁷ on

¹⁷ Paul, J. W., Hsley, L. C., and Gleim, E. J., Flame safety lamps: Bull. 227, Bureau of Mines, 1924, 212 pp.

its flame indicates the presence of such an amount; but in places where the safety lamp fails to indicate gas, mine officials are ignorant of the actual percentage which may be present. When the fact becomes better appreciated that enough methane is always present in some mines to make a dangerous condition should a fan stop suddenly, or should the ventilating system be deranged, more care will probably be taken to ascertain the amount of the gas in individual mines.

The Burrell methane indicator,¹⁸ a portable device for giving the percentage of methane below that at which the safety lamp gives an indication, was developed at the Pittsburgh experiment station of the Bureau of Mines. It will detect methane when present in amounts greater than about 0.1 per cent. This device, however, is not intended to displace gas analysis in the study of mine ventilation, but rather to fill the gap between the safety lamp and precise gas analysis.

Regular analyses of samples taken from the ventilating current in different sections of a mine, such as the main returns, the splits, and the goave, and at the face, will indicate whether there is danger of a fire-damp explosion. If a split ventilating a certain section of a mine contains a large amount of methane at any time, more air can be forced through that part with consequent decrease in the amount of air passing through a less gaseous district, thereby equalizing conditions. As a final resort it may be possible to increase the total quantity of air passing through the mine. In some mines much of the methane found in the returns is liberated only in certain sections. Systematic analyses of the air in different parts of the mine will define these sections. Curves may be drawn to show the percentage of methane produced each day in certain areas, and a rule can be established that a certain maximum of methane shall not be exceeded.

VERIFYING SAFETY-LAMP TESTS

Gas analysis is also useful at the mine for checking the degree of accuracy with which fire bosses and other employees can determine percentages of methane by means of the safety lamp. Great difference of opinion exists as to the exact proportion detectable under the same conditions. Some men use a high flame, whereas the majority lower the flame for cap indications; but the results are seldom verified at the mine by analyses of the particular mixture examined. The kind of lamp, the illuminant used, and many other factors may affect the height of the cap. Under exactly the same

¹⁸ Burrell, G. A., A new fire-damp indicator: *Coal Age*, vol. 9, 1916, p. 157. Milligan, L. H., A critical study of the Burrell indicator for measuring combustible gases in air: *Tech. Paper 357, Bureau of Mines, 1925, 40 pp.*

conditions, with small percentages of methane present, one observer may see a cap distinctly, although another with less acute vision may not. A series of analyses of mixtures examined by safety lamps will show clearly what may be expected from the lamps.¹⁹ Since the fact has been recognized that percentages of methane much below that required to form an explosive mixture with air may contribute to disastrous dust explosions, urgent need has been felt for the detection of smaller quantities of methane than are generally detected by the use of a safety lamp.

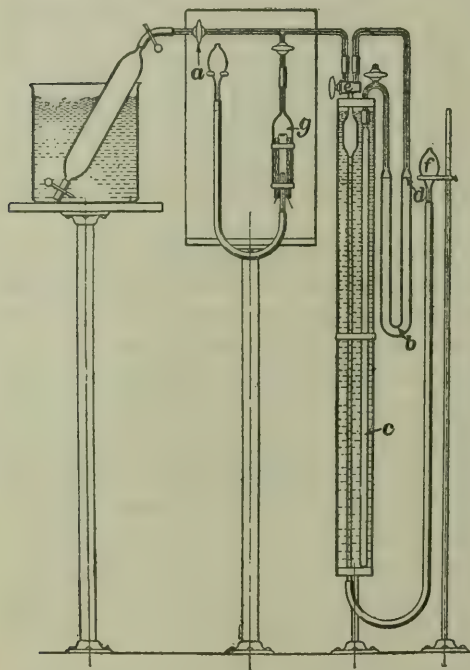


FIGURE 6.—Laboratory apparatus for exact determination of methane. For explanation, see text

HALDANE APPARATUS FOR PRECISE ANALYSIS OF METHANE

The apparatus shown in Figure 6 includes a 21-c. c. burette similar to that used on Haldane's apparatus; the bulb has a capacity of 15 c. c. and the stem a capacity of 6 c. c. The stem is graduated in hundredths of a cubic centimeter. The burette has an attachment that compensates for slight changes in room temperature during an analysis and facilitates the taking of readings. The slow-combustion pipette *g* is similar in construction to the pipette shown in Plate III (p. 18).

At the laboratory the sample container is set up as shown. To make an analysis proceed as follows: Draw about 10 c.c. of the sample into the burette and discharge it through the three-way cock *a*, sweeping the air out of the capillary tubing; then draw about 21 c.c. of the sample into the burette and measure it against the pressure in the compensating tube *c* by means of the liquid in the manometer *b*. With this apparatus use a mixture of one part of glycerin and three parts of water in the manometer. Such a mixture responds readily to slight movement of the mercury in the burette. Because of its comparatively low density, water alone is unsatisfactory when the burette contains mercury. Although the compensating device is

¹⁹ Paul, J. W., Ilsley, L. C., and Gleim, E. J. Work cited.

similar in principle to that shown attached to the burette in Plate III, it is operated differently. Put enough glycerin solution in manometer *b* (fig. 6) to bring the surface of the liquid in both parts of the U tube approximately on a line with the scratch mark shown at *d*. After the sample has been drawn into the burette turn the burette stopcock *e* so that communication is made between the burette and the manometer. Slightly raise or lower the leveling bulb *f*; then movement of the mercury brings the glycerin solution in the U tube exactly to the mark *d*. Next take the burette reading.

After the gas has been measured in the burette pass it into the slow-combustion pipette and heat the platinum wire. After combustion allow the pipette to cool and return the gas to the burette in order to measure the contraction in volume that results from the burning of the methane. This contraction, divided by 2 and calculated to a percentage basis, represents the proportion of methane in the mine air.

As stated above, methane is the combustible gas commonly found in mines. Traces of gaseous paraffins higher than methane have not been positively identified in normal mine air examined by the authors.

As the sample is drawn through the horizontal capillary tubes leave a small amount therein, but after measurement pass it into the combustion pipette and do not withdraw until combustion is complete. A small amount of gas in excess of that measured in the burette and equal to the amount introduced into the capillary train will therefore remain unburned. This method avoids the small error that would follow if the sample was passed back and forth between the burette and the combustion pipette during combustion. The error would, however, ordinarily be small enough to neglect.

An analysis does not take longer than 10 minutes, and determinations of the same sample agree within 0.01 or 0.02 per cent.

PORTABLE APPARATUS FOR THE DETERMINATION OF METHANE IN MINE AIR

Figure 7 shows a portable apparatus for the determination of methane in mine air. The burette has a capacity of 50 c. c.—the bulb 45 c. c., and the stem 5 c. c.—and is graduated in five-hundredths of a cubic centimeter. To simplify the apparatus, water slightly acidified with sulphuric acid is used in the burette and the combustion pipette. Determinations of methane may be made with an accuracy of 0.1 per cent when the analyses are properly made, and the burette is drained carefully each time before readings are taken.

To make an analysis, draw the sample into burette *a* (fig. 7) through *c*, and measure its volume at atmospheric pressure by hold-

ing the surface of the water in the level bottle of the burette on a line with the surface of the water in the burette. Pass the sample into the combustion pipette *b*, and heat the platinum wire a bright yellow. After about 2 minutes the methane in the sample is completely oxidized. Let the pipette cool and transfer the gas to the burette, where the contraction in volume due to the burning of methane is measured in the same way as the sample was originally measured. The contraction in volume, divided by 2, gives the amount of methane originally present in the sample.

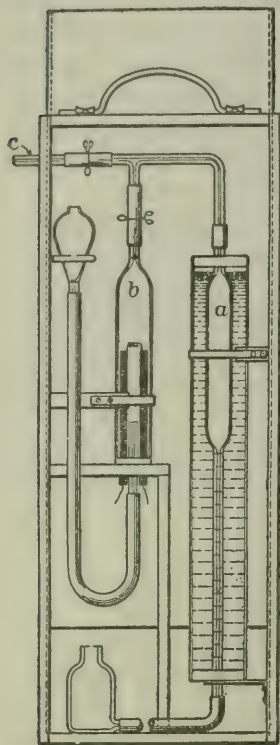


FIGURE 7.—Portable apparatus for determination of methane in mine air. Capacity of burette, 50 c. c.; capacity of bulb of burette, 45 c. c.; capacity of stem of burette, 5 c. c.; stem graduated in 0.05 c. c. For explanation, see text

Many coal mines normally contain less methane in the workings than a device of the degree of accuracy of this can measure, but, on the other hand, there are mines where the amount of methane, even in the main returns, never falls below 0.2 to 0.5 per cent. The value of the apparatus lies in its ability to detect proportions of methane that are much below those detectable by the safety lamp and are far below the explosive proportion. Because of its ease of manipulation and simplicity the apparatus may appeal to the officials of mines where the employment of a chemist is not feasible.

The following methane determinations were obtained with the apparatus by a person who was not a chemist and who had never before made analyses of gases or other substances. The sample of mine air actually contained 0.33 per cent of methane, as shown by a more exact laboratory analysis.

Results of methane determinations of a mine-air sample

Sample No.	CH ₄ , per cent	Sample No.	CH ₄ , per cent
1	0.30	11	0.36
2	.30	12	.35
3	.39	13	.36
4	.30	14	.40
5	.35	15	.33
6	.26	16	.33
7	.30	17	.33
8	.24	18	.26
9	.30	19	.30
10	.40	20	.26

USE OF A STORAGE BATTERY OR RESISTANCE BANK

A storage battery can be used for heating the No. 30 platinum wire to incandescence. A battery that will produce an electric current of 4 amperes at 5 volts is required. Dry cells such as are used with house doorbells may be utilized, but they are not as suitable because they are not intended for continuous service of 2 minutes at a time. Some electric cap-lamp batteries now on the market are suitable. The most satisfactory arrangement will result when a lamp bank or other form of resistance that can carry 4 or 5 amperes is connected to an electric lighting circuit and set up at the headquarters selected for the work; the samples are carried or mailed to this place for analysis. When the air in a large number of mines is being sampled for methane, a resistance bank can be installed at each mine if electricity is used there, and the apparatus for gas analysis can be carried from place to place; a series of samples can then be collected and analyses made at the particular mine where the samples were gathered.

PORTABLE APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE AND METHANE

Figure 8 shows a portable apparatus for methane determinations. It is similar to that in Figure 7, except that a caustic potash pipette, *b*, is included for the determination of carbon dioxide. Water is used in the burette and the combustion pipette. The apparatus is operated like that shown in Figure 7, except that the sample after measurement in the burette and before burning is passed into the potassium hydroxide pipette *b* for the removal of carbon dioxide. The two determinations can be made with an accuracy of 0.1 per cent.

Samples that are to be analyzed for their carbon dioxide content should be collected by air displacement by one of the methods already described. The use of water in the burette of the apparatus shown in Figure 8 does not, however, militate against correct determination of the carbon dioxide, at least within the experimental error

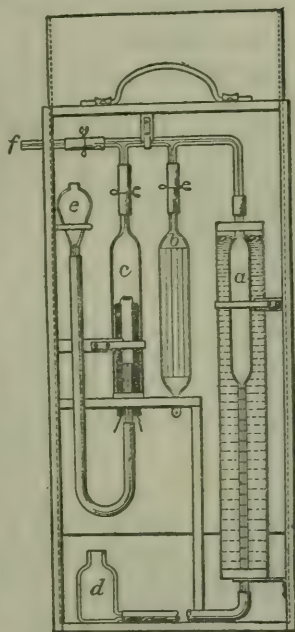


FIGURE 8.—Portable apparatus for determination of carbon dioxide and methane in mine air. Water to be used in burette and combustion pipette. Capacity of burette, 50 c. c.; capacity of bulb of burette, 45 c. c.; capacity of stem of burette, 5 c. c.; stem graduated in 50 c. c. For explanation, see text

of reading the burette. To prove this fact some experimental work was performed in which definite quantities of carbon dioxide were added to air in bottles. The samples were then analyzed, first by means of the apparatus, shown in Plate III, in which mercury is used in the burette, and then by means of the apparatus, shown in Figure 8, in which water is used. Two or more analyses were made of each sample. The results appear in the following table. The percentages of carbon dioxide found with the apparatus shown in Plate III are given in column A; those found with the apparatus shown in Figure 8 appear in column B:

Carbon dioxide found with two types of apparatus

Series	A	B	Series	A	B
	<i>Per cent</i>	<i>Per cent</i>		<i>Per cent</i>	<i>Per cent</i>
No. 1.....	0.73	0.82	No. 3.....	0.47	0.41
	.73	.71		.45	.43
		.71		.45	
		.90	No. 4.....	.28	.40
		.90		.27	.30
		.91			
No. 2.....	.67	.76			
	.68	.67			

SIMPLE PORTABLE GAS-ANALYSIS APPARATUS FOR COMPLETE ANALYSIS OF MINE AIR

Figure 9 shows a modified Orsat apparatus that is simple in operation and can be used where great accuracy is not desired.²⁰ With this apparatus carbon dioxide and carbon monoxide can be determined to within about 0.2 per cent, and methane and hydrogen can be determined almost as accurately by calculation from the combustion data.

APPARATUS

The apparatus consists essentially of the burette *e* and the four pipettes *a*, *b*, *c*, and *d*. The burette has a capacity of 100 c. c. and is graduated in 0.2 c. c. The pipettes contain: *a*, Potassium hydroxide solution for the removal of carbon dioxide; *b*, alkaline pyrogallate solution for the removal of oxygen; and *c*, ammoniacal or acid cuprous chloride solution for the removal of carbon monoxide. At *d* is the slow-combustion pipette for burning the methane; it contains distilled water slightly acidified with sulphuric acid. The pipettes *a*, *b*, and *c* are provided with glass rods (not shown in sketch) to increase the absorption surface of the reagents. The platinum wire inside the combustion pipette is No. 30 (B. & S. gauge), is supported by two pieces of glass tubing, and is sealed to copper wires that pass through the glass tubes.

²⁰ Burrell, G. A., and Seibert, F. M., Gas analysis as an aid in fighting mine fires: Tech. Paper 13, Bureau of Mines, 1912, pp. 14-15.

MEASUREMENT

There are two leveling bottles, *f* and *g*, which are manipulated as follows: Before an analysis is begun, bring the solutions in pipettes *a*, *b*, *c*, and *d* exactly to the marks on the capillary glass tubes of the pipettes by use of the leveling bottle connected to the burette. Close the stopcocks, as shown in the sketch. To draw a sample of gas into the burette, raise the acidulated water in the latter to the point marked *h* on the capillary tube by raising the leveling bottle, opening the stopcock *i* to the air, and finally when the water is at the desired point by again closing *i*. Make a rubber connection between *i* and the sample container and place the latter in a vessel of water. Open the connections, including the stopcocks or pinchcocks on the sample container and the stopcock *i*, and lower the leveling bottle until the water in the burette is brought to the lowest division on the burette. Close stopcock *i* to the outside air and measure the gas sample in the burette at atmospheric pressure by holding the leveling bottle in such a position that the surface of the water in it is on a line with the surface of the water in the burette. Allow 1 minute after the sample is brought into the burette before taking the measurement in order to guard against a small error which would result if time was not allowed for drainage of water down the sides of the burette.

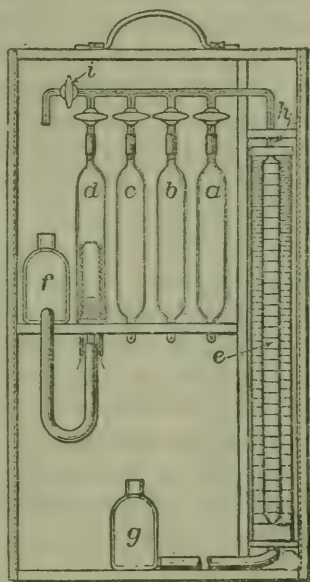


FIGURE 9.—Modified Orsat gas-analysis apparatus. For explanation, see text

DETERMINATION OF CARBON DIOXIDE

After measurement pass the sample into pipette *a* in order to remove carbon dioxide. To do this, pass the sample back and forth several times between the pipette and the burette. Bring the solution in the pipette *a* exactly to the mark on the capillary stem and measure the sample again, allowing 1 minute for drainage. The loss in volume shows the amount of carbon dioxide originally present in the gas sample.

DETERMINATION OF OXYGEN

Now pass the sample into pipette *b* for the removal of oxygen. Manipulate in the same manner as in determining carbon dioxide.

Alkaline pyrogallate solution does not remove oxygen from a gas mixture as rapidly as caustic potash solution removes carbon dioxide; consequently longer contact must be allowed between this solution and the sample.

DETERMINATION OF CARBON MONOXIDE

After the sample in the burette has been measured again and the contraction in volume due to the absorption of oxygen has been recorded, pass it into pipette *c* for the removal of carbon monoxide.

Cuprous chloride is not as satisfactory an absorbent for carbon monoxide as alkaline pyrogallate solution is for oxygen, especially when the solution is confined in an Orsat pipette and the absorption is conducted under the conditions mentioned.

Absorption of the gas in any pipette may usually be considered complete when no difference in volume of the sample is observed after successive passages of the gas mixture into the pipette.

Attention should be called to the fact that if carbon dioxide is not removed by caustic potash solution it will be absorbed by alkaline pyrogallate solution, and if this solution does not entirely remove the oxygen the latter will be absorbed to some extent by the cuprous chloride solution; hence it is absolutely necessary to remove completely each constituent in the particular pipette in the order provided for its removal before the gas mixture is passed into the next pipette.

COMBUSTION

After those constituents of a gas sample that are absorbable by the reagents are removed, dilute the sample with air, if it contains less than an explosive proportion of methane, by lowering the leveling bottle connected to the burette, opening the stopcock *i* to the outside air, and drawing some of the latter into the burette, so that the combined volume of air and residual gas shall be from 98 to 100 c. c. Pass the measured mixture into the slow-combustion pipette *d* and bring the platinum wire therein to a bright-yellow heat. Allow the wire to remain hot for 2 minutes. After pipette *d* has become cool to the hand, withdraw the sample into the burette and determine the contraction in volume due to the burning of the methane. Pass the sample into pipette *a*; the caustic potash solution absorbs the carbon dioxide produced by the burning of the methane. Return the sample to the burette and record the contraction in volume caused by this absorption. The carbon dioxide produced by the burning of the methane should be equal to one-half the contraction. If this relation does not hold good within 0.2 or 0.3 c. c., some other combustible gas is present in addition to methane or an error has been made in the manipulation of the apparatus.

Finally, pass the sample into alkaline pyrogallate pipette *b* to make sure that enough oxygen had been present for complete combustion of the methane.

If 100 c. c. of the sample is taken for analysis and the analysis is made according to the direction given above, the amount of each absorption in pipettes *a*, *b*, and *c* shows directly the percentage of carbon dioxide, oxygen, and carbon monoxide present. The carbon dioxide produced by the burning of the methane is also a direct measure of the percentage of the methane originally present in the sample. When less than 100 c. c. of the sample is taken for analysis, a simple calculation to a percentage basis shows the quantity of each constituent present. If the sample contains more than an explosive proportion of methane, handle the residual gas as follows after the absorbable constituents have been removed by pipettes *a*, *b*, and *c*:

Pass the residual gas directly into pipette *d* and bring the platinum wire therein to a white heat. Measure enough oxygen or air in burette *e* to burn the sample completely and pass it into pipette *d* at the rate of about 10 c. c. per minute. The methane burns as the methane and oxygen come in contact with the hot wire, and an explosion caused by the accumulation of methane and oxygen can not follow.

When combustion analyses are performed with the apparatus, place a wire screen around pipette *d*, so that, if an explosion shatters the glass, flying pieces will not cause injury. This precaution should be taken whenever combustion analyses are made in any gas-analysis apparatus.

PRECAUTIONS

Two or three trials may be necessary before mixtures which contain unknown and large proportions of methane can be handled to the best advantage. The apparatus is accurate to about 0.2 or 0.3 per cent, but good results can be obtained only by the strictest attention to details. Keep solutions fresh, see that the rubber tubing is in good condition and free from leaks, and lubricate all stopcocks well. Never draw the solutions in pipettes *a*, *b*, and *c* into the capillary train above the stopcocks; otherwise the analysis may be worthless.

Carbon monoxide is absent from normal mine air and air typifying mine conditions other than those caused by fires, explosion, or after blasting; consequently, pipette *c* need not be used in analyzing many samples of mine air.

Rubber bags are provided which are fastened to the reservoir bulbs of the pipettes *a*, *b*, and *c*. These bags should not be removed, and should be examined frequently in order to make sure that the

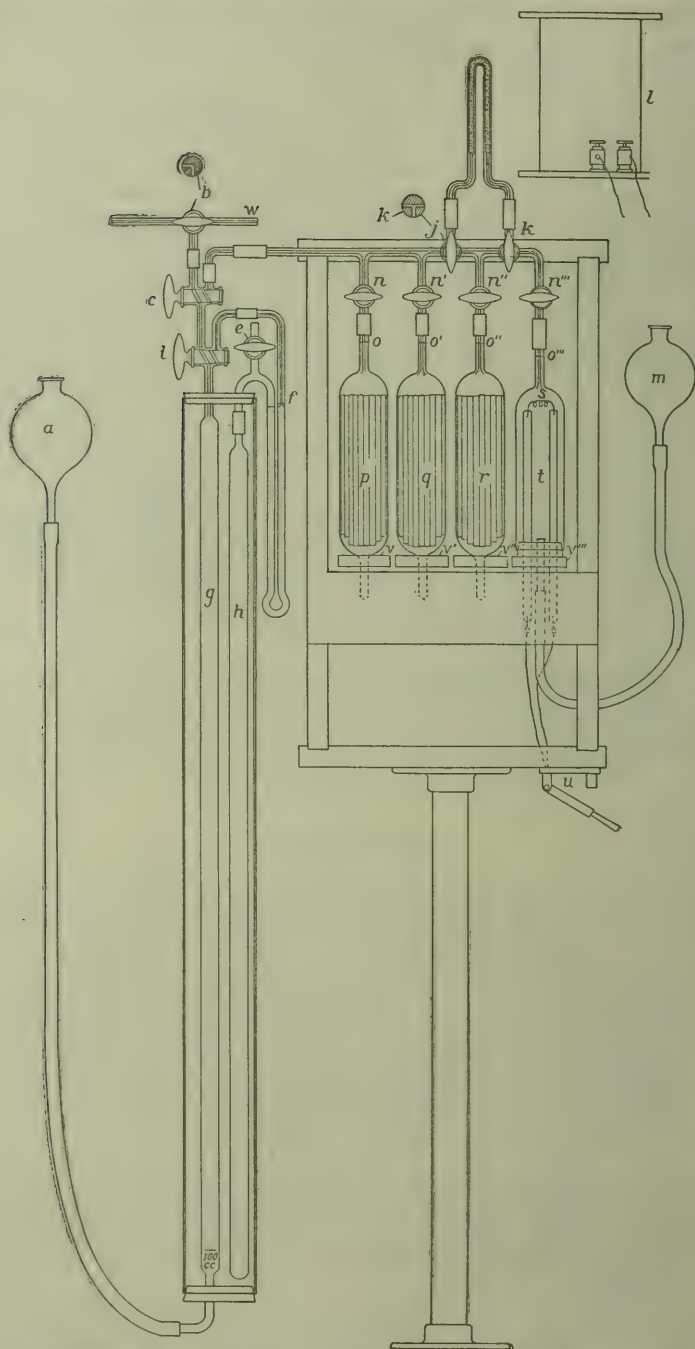


FIGURE 10.—Copper oxide apparatus for complete analysis of gases. For explanation, see text

rubber stoppers are tightly in place and that the bulbs do not leak at any point.

It will be found advisable occasionally to run some of the acidified water from burette *e* through the horizontal capillary train and out through *i* to neutralize any caustic potash that may have accidentally found its way from pipettes *a* and *b* into the train.

COPPER OXIDE APPARATUS FOR COMPLETE ANALYSIS OF GASES

The Haldane apparatus previously described is intended for use in analyzing gas mixtures that do not contain large enough proportions of any constituents to cause the mercury to rise, during an analysis, to the ungraduated part of the burette where readings can not be made.

The authors have found that an apparatus of the type shown in Plate III can be used for the analysis of many normal or abnormal mine atmospheres. However, many samples containing large proportions of various constituents are analyzed at the laboratory of the Bureau of Mines with an apparatus of the type shown in Figure 9. Such mixtures include illuminating gas, oil gas, mine gas high in methane, natural gas, exhaust gases from gasoline locomotives, and special samples prepared during experimental work in the bureau's laboratory.

ADVANTAGES OF APPARATUS

The apparatus shown in Figure 10 and Plate V was assembled to contain in one device for general use the desirable features found in several types of gas-analysis apparatus already on the market. These features follow:

1. Mercury in the burette and the combustion pipette.
2. A compensating device, *h*, allowing small changes in the temperature and pressure of the room during the course of the analysis to be disregarded.
3. A water jacket.
4. Slow-combustion method for making combustion analyses.
5. Copper oxide for the fractional combustion of carbon monoxide and hydrogen. This eliminates three pipettes and makes the apparatus more compact. Time is saved because there is no need to prepare cuprous chloride and colloidal palladium solutions, and the effect of solubility of hydrocarbons of high molecular weight is reduced to a minimum. Ethane and propane are soluble to some extent in cuprous chloride solutions.
6. Adjustable brackets for supporting each pipette. It is easy to make close connections between the train and pipettes if the brackets

are adjustable. The pipettes are easily removed for cleaning and refilling.

7. Assembling of the apparatus in a common train to avoid entirely making and breaking connections, which is necessary when pipettes are connected in turn to the burette for absorptions and to the combustion pipette for burning.

8. A second three-way stopcock, *c*, sealed to the burette, so that a gas sample can be taken into the burette at the top without disconnecting the burette from the train of pipettes.

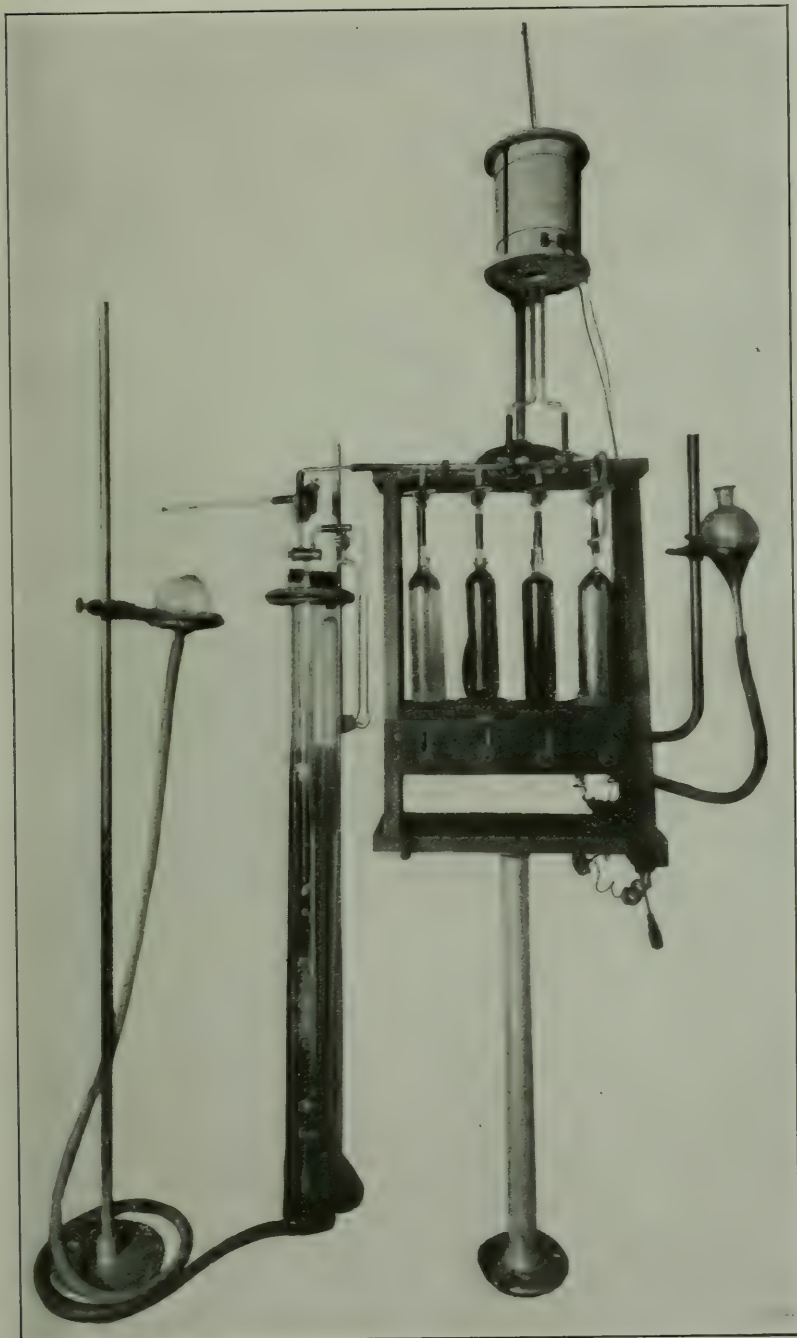
The burette of the apparatus is graduated in tenths of a cubic centimeter from the upper stopcock down to the 100-c. c. mark, so that the quantity of gas measured is the quantity of gas analyzed.

REASONS FOR DISCARDING THE EXPLOSION PIPETTE

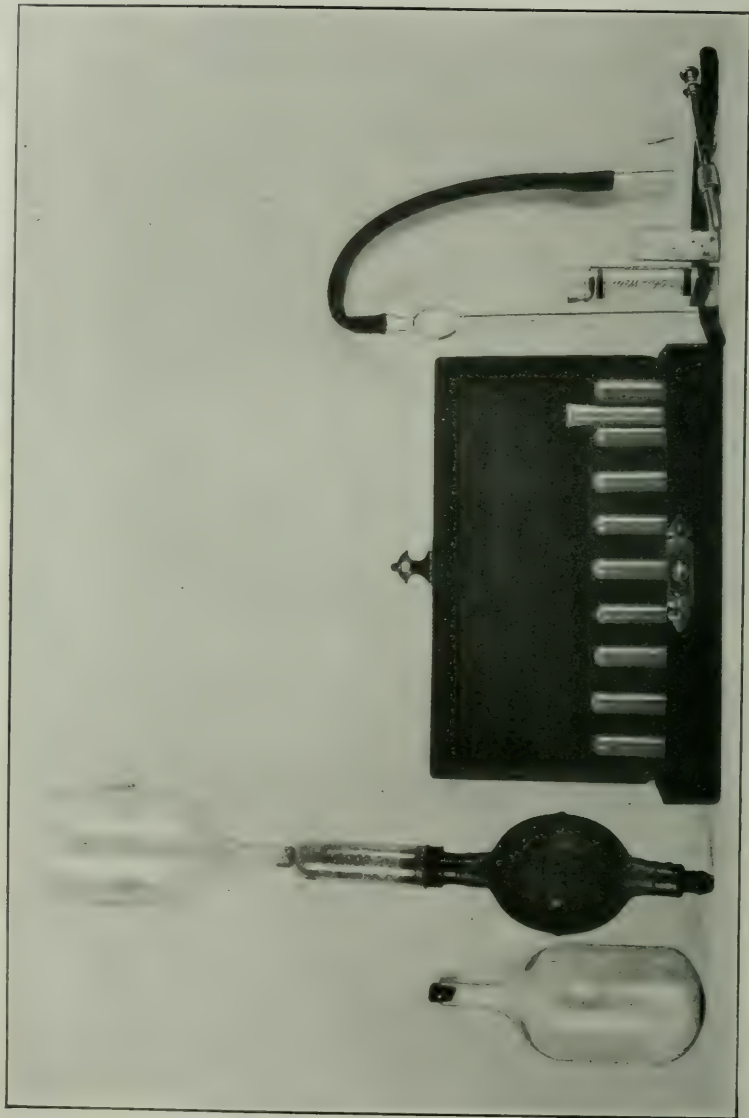
The explosion method of determining the combustible constituents was discarded because of the following objections:

Many gas mixtures analyzed at the bureau's laboratory do not contain explosive gases in large enough quantity to produce an explosive mixture with air; consequently, if the explosion method is used, hydrogen or electrolytic gas (hydrogen and oxygen made by the electrolysis of water) must be added to make the mixture explosive. This procedure introduces an additional factor in the preparation and measurement of the exciting gas. Furthermore, when the explosion method is employed small quantities of gas mixtures that contain a large proportion of methane or of the higher-paraffin hydrocarbons have to be used. This requirement applies especially to natural gas, in which the paraffin hydrocarbons predominate; to many special mixtures prepared in the laboratory; and also to mine atmospheres containing a large proportion of methane. For instance, when methane-air mixtures are ignited by an electric spark they have explosive limits approximately as follows: Low, 5.5 per cent methane; high, 14.5 per cent methane; and most violent, 9.5 per cent methane. To remain within the explosive limits of the mixtures and to avoid too violent an explosion, only a small quantity of gas can be taken for an explosion, and any error of manipulation or error inherent to any type of apparatus is multiplied 8 or 10 times when the calculations of results is made to a percentage basis.

The use of the explosion method also demands exceptionally tight connections on the explosion pipette to resist the pressure of the explosion. With the slow-combustion pipette there need not be heavy pressure at any time on connections and faulty analyses caused by loss of the sample through leaks are largely avoided.



COPPER OXIDE APPARATUS FOR COMPLETE ANALYSIS OF GASES



STANDARDS AND APPARATUS FOR DETERMINING PERCENTAGE OF SATURATION OF CARBON MONOXIDE IN BLOOD, AND THE ANALYSIS OF MINE-AIR SAMPLES FOR CARBON MONOXIDE CONTENT, BY PYRO-TANNIC ACID METHOD

DESCRIPTION OF APPARATUS

Many modifications of the original Orsat apparatus for gas analysis are used at present; each has particular merits and is adapted for some special work. The number and kind of pipettes used depend upon the composition of gas to be analyzed. If ethane is to be determined, a copper oxide tube is required (fig. 10) and

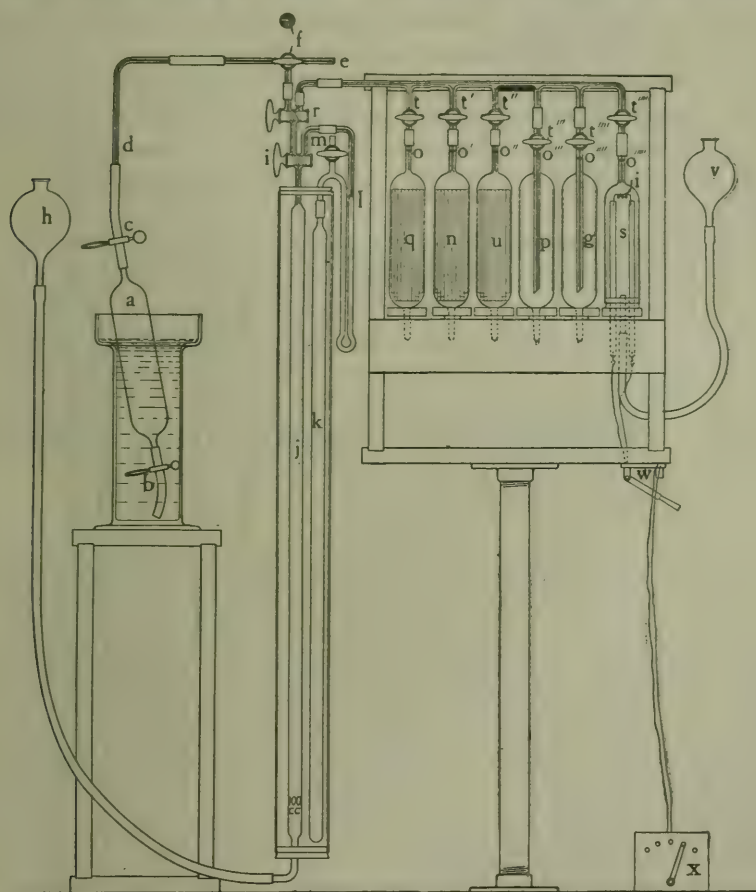


FIGURE 11.—Orsat apparatus for complete analysis of gases which do not contain ethane or other higher saturated hydrocarbons. For explanation, see text

the cuprous chloride pipettes are omitted, as carbon monoxide is determined by combustion along with the hydrogen. If ethane is absent, as in producer and blast-furnace gases, two cuprous chloride pipettes may replace the copper oxide tube (fig. 11), and the methane and hydrogen are determined from the combustion data by

means of the formulas given under "calculations for determining combustibles," page 26.

The Orsat apparatus²¹ is used in the Bureau of Mines gas laboratory at Pittsburgh for complete and partial analyses of gases. A complete analysis of carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, and ethane can be made without connecting or disconnecting any parts. Because all of the constituents are removed before the paraffin hydrocarbons are burned, larger amounts of these constituents may be taken for combustion with oxygen and more accurate determinations of methane and ethane may be made. The same argument holds for hydrogen and carbon monoxide, which are determined by fractional combustion with copper oxide at 300° C. Mercury is used in the burette as the confining liquid.

The apparatus arranged for complete gas analysis is shown in Plate V and Figure 10. It consists essentially of a 100-c. c. water-jacketed burette, *g*, with a Pettersson compensating tube, *h*, for correcting for changes of temperature and pressure during the analysis; four pipettes, *p*, *q*, *r*, *t*, and a copper oxide tube, *i*, with an electric heater, *l*, for the fractional combustion of hydrogen and carbon monoxide. The manometer on the compensator is filled with mercury or a 1 to 3 glycerin-water solution to the mark *f*.

BURETTE

Figure 12 gives details of the burette, which is graduated to 0.1 c. c., every tenth mark extending half-way around the burette. The even cubic centimeters are etched on the burette and the 100-c. c. mark is placed at the bottom. In preparing the apparatus for use proceed as follows: Fill the simple absorption pipettes *p*, *q*, and *r* with pieces of hollow glass tubes as usual. Pipette *p* contains caustic solution for the removal of carbon dioxide; *q* contains fuming sulphuric acid for removal of illuminants; and *r* contains alkaline pyrogallate solution for oxygen. Place enough reagent in the pipettes so that when they are drawn to the marks *o*, *o'*, and *o''*, enough reagent remains in the rear branch of the pipette to form a seal. Attach rubber bags to the rear branches of pipettes *q* and *r*, to prevent access of air to the reagents. Inflate each bag slightly before attaching it to the pipette.

²¹ Burrell, G. A., and Oberfell, G. G., The use of copper oxide for fractionation, combustion of hydrogen, and carbon monoxide in gas mixtures: Jour. Ind. Eng. Chem., col. 8, 1916, p. 228. Jones, G. W., and Neumeister, F. R., An improved Orsat apparatus for gas analysis: Chem. and Met. Eng., vol. 21, 1919, p. 734.

Bul-42

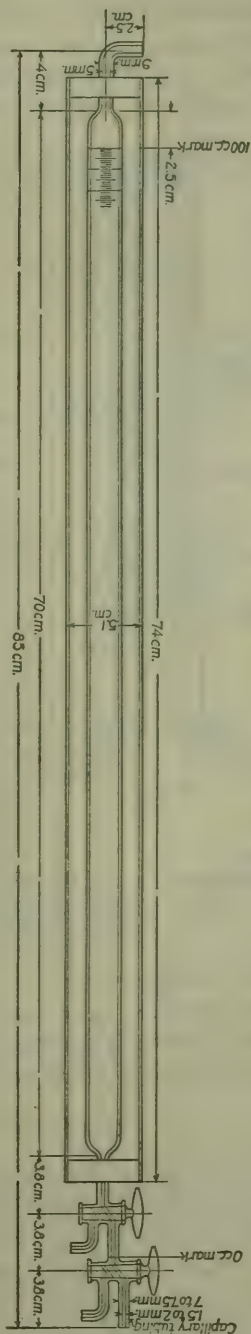


FIGURE 12.—Details of standard burette, model C

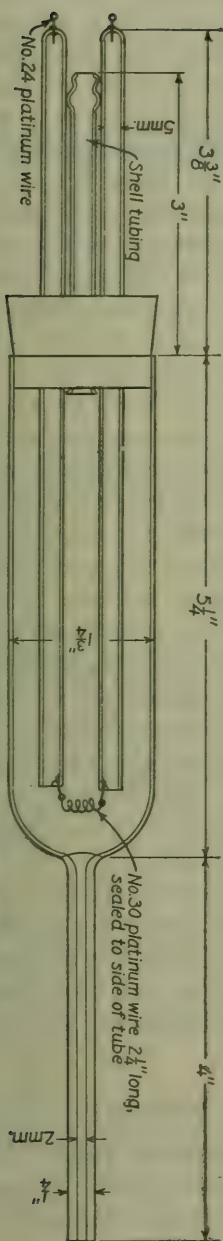


FIGURE 13.—Details of combustion pipette for Orsat apparatus

SLOW-COMBUSTION PIPETTE

Methane and ethane are determined by slow combustion in pipette *t*, which contains *s*, a $2\frac{1}{4}$ -inch coil of No. 30 (B. & S. gauge) platinum wire. Insert the ends of *s* in the tops of two glass tubes extending through the rubber stopper in the bottom of the pipette.

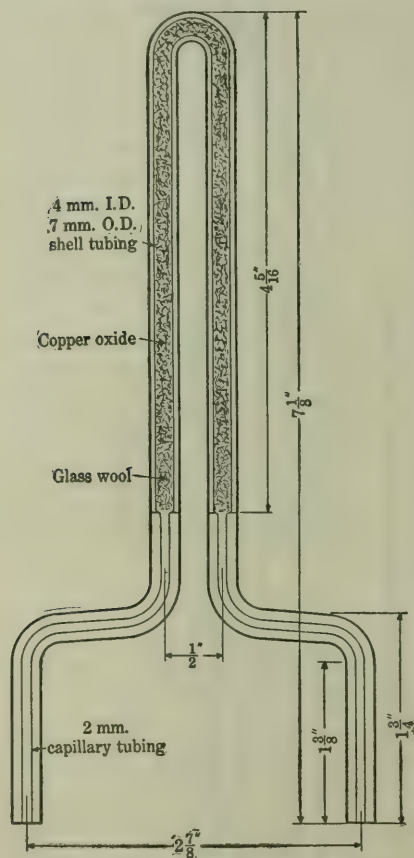


FIGURE 14.—Details of copper oxide tube

After the pipette is mounted in place, pass mercury into the bulb *m* until the pipette is filled to the mark *o'''*.

(See fig. 13.) Seal stout loops of platinum wire into the bottoms of these tubes. For 110-volt alternating current connect these loops to the secondary of a 150-watt toy transformer, which has a variable voltage ranging from 1.5 to 30 volts. Stretch a piece of No. 22 (B. & S. gauge) nichrome wire about 16 inches long between two binding posts mounted on the bottom board of the wood frame above the switch *u*. Connect the binding post at one end of this wire and a sliding contact on it to the circuit, to permit close adjustment of the temperature of the platinum coil. A rough adjustment is made in steps on the transformer. The wire mentioned above requires about 6 volts. Use mercury for the confining fluid in the slow-combustion pipette.

Before the pipette is assembled fill the glass tubes in the combustion pipette *t* with mercury to complete the electrical circuit.

COPPER OXIDE TUBE AND MANIFOLD

Figure 14 gives details of the copper oxide tube. Bend thin-walled glass tubing, preferably pyrex, 4 mm. inside diameter, into the form of a U. Cut it off to comply with the dimensions given in the figure, and fill it with about 3.5 grams of fine wire copper oxide containing a few particles of metallic copper. The oxide is held in place by small plugs of glass wool at both ends of the tube. Seal

capillary tubing of 1.5 mm. internal diameter to the ends of the thin-walled U tube for connection to the manifold at the stopcocks *j* and *k*.

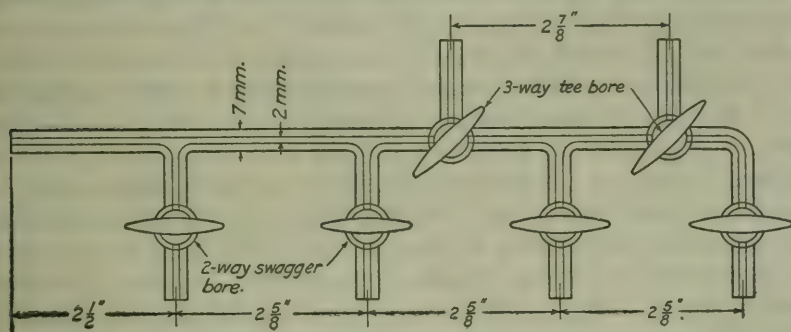


FIGURE 15.—Manifold for Orsat apparatus

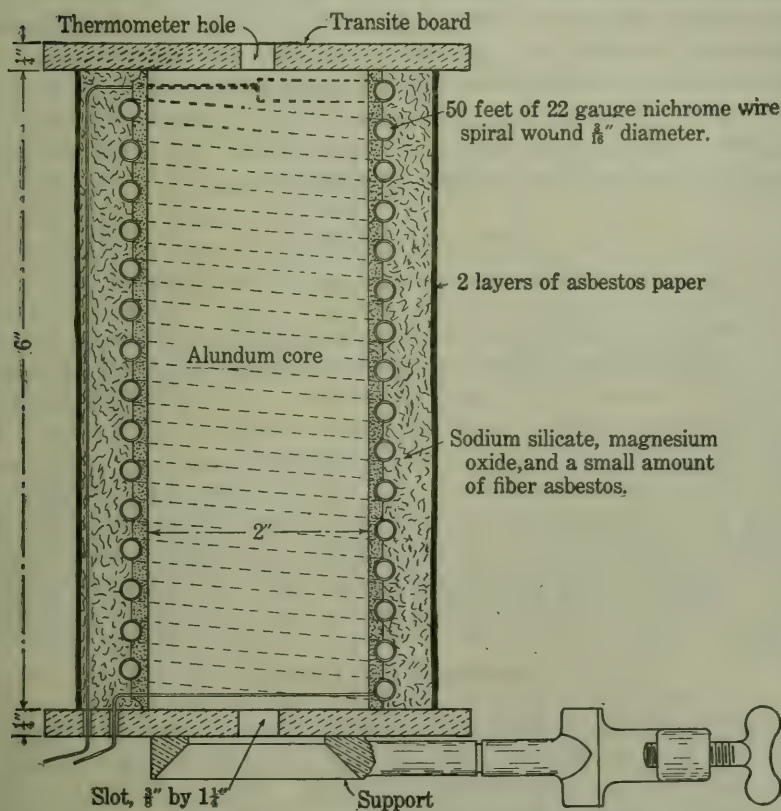


FIGURE 16.—Electric heater for copper oxide tube

(See fig. 15.) The entire free space of the U tube from one stopcock to the other should not exceed 2.5 c. c.

ELECTRIC HEATER

Figure 16 shows the construction of the electric heater for raising the temperature of the copper oxide to 300°C . The heating element is made of 50 feet of No. 22 (B. & S. gauge) nichrome wire, wound in a helical coil. This element is easily made by using a lathe to wind the wire on a spindle three-sixteenths inch in diameter, and then coiling the helix around a grooved alundum tube of 2 inches internal diameter. Adjacent coils should be far enough apart for ample electrical insulation. Heat insulation is obtained by covering the outside of the heating element with a 1-inch layer of a mixture of magnesium oxide, asbestos fiber, and sodium silicate. The outer covering may be layers of asbestos paper or sheet metal. Close the ends with circular pieces of transite board held together by stay-bolts, as shown. Bring out the two ends of the wire coil to two binding posts mounted on the base of the heater. Before use, dry the furnace thoroughly for several hours at 100°C . The winding described is for use with 110-volt current, and will raise the temperature to 300°C . in 15 minutes, when a current of 1.1 amperes is used. When this temperature is attained reduce the current to about 0.7 ampere by use of a 50-ohm slide-wire rheostat. Insert a thermometer through a small hole in the top of the furnace.

OPERATING PROCEDURE

TESTING APPARATUS FOR TIGHTNESS

To test the apparatus for leaks, draw into the burette about 50 c. c. of air and turn cock *c* (fig. 10) to connect with the manifold (glass assembly through which gas is distributed to the different pipettes of the apparatus, fig. 15). Raise mercury-leveling bulb *a* so as to place the gas under 8 inches or more of mercury pressure. Any leaks in the stopcocks or rubber connections are shown by the mercury rising slowly in the burette. This, however, does not indicate the tightness of the rubber connections below stopcocks *n*, *n'*, *n''*, and *n'''*. Leaks at these connections are shown by the solutions falling from marks *o*, *o'*, *o''*, and *o'''* after they have been standing a short time.

MEASURING THE SAMPLE

Before a series of analyses is begun adjust the gas in the compensator tube to atmospheric pressure by momentarily removing three-way cock *d* and compensator cock *e*. Adjust all the reagents in the absorption pipettes and the mercury in the combustion pipette to the marks on the capillaries. Sweep the manifold and U tube *i* free of oxygen or residual gas from a previous determination by drawing a sample of air into the burette and passing it into the alka-

line pyrogallate pipette *r* to remove the oxygen. Then pass this residual nitrogen through the copper oxide tube *i* and pipettes *p*, *q*, and *t* to sweep out the remaining oxygen, which may have been contained therein. Much time can be saved by having a supply of nitrogen at hand for sweeping out the manifold and capillaries.

With the heater *l* raised above the copper oxide tube, switch on the current, and regulate the resistance so that the furnace will be at the desired temperature (about 300° C.) by the time the fractional combustion of the hydrogen and carbon monoxide is to be made. Turn stopcocks *d*, *c*, and *b* to communicate with the outside air at *w*. Raise leveling bulb *a* until the mercury reaches *b*. By means of a suitable capillary tube connect the sample of gas to be analyzed to the left branch of the three-way cock *b* and turn *b* to communicate with the sample. Lower leveling bulb *a*, drawing about 20 c. c. of gas into the burette. This sample is contaminated with air from the connections. Discard it by turning cock *b* to connect with *w*, and raise the leveling bulb *a*, expelling the gas at *w*. When the mercury reaches *b*, turn *b* to communicate again with the sample, and draw 50 to 60 c. c. of the gas into the burette as previously directed. Turn cock *c* through 180°, making connection with the manifold leading to the pipettes and turn *b* to connect with the air at *w*. Read the volume of gas by turning cock *d* through 180°, communicating with the compensator *f*. Raise or lower the leveling bulb *a* until the mercury in the compensator comes to mark *f*. As the burette contains a measured quantity of sample and the fluids in the pipettes have been adjusted to the marks on the capillaries, and the cocks *n*, *n'*, *n''*, *n'''*, *j*, and *k* closed with respect to the capillary train, the sample is ready for analyses.

CARBON DIOXIDE

Raise leveling bulb *a* slightly to put the gas under slight pressure and avoid any possibility of pulling the caustic solution into cock *n* and the manifold, then turn cocks *d* and *n* to admit the sample from the burette to caustic pipette *p*; continue raising *a* until the mercury reaches *d* and lower the leveling bottle, drawing the gas back into the burette until the level of the caustic solution covers the glass tubes in the pipette; again pass the gas four times into the caustic pipette, and return it to the burette in the same manner. On the last pass, return the gas to the burette, bringing the level of the reagent to mark *o* very carefully to avoid getting any solution into the stopcock and the manifold. Close stopcock *n*, turn *d* to communicate with the compensator, and adjust the mercury level in compensator manometer to mark *f*. Read and record the contraction. The analyst, unless he is familiar with the gas and knows that the solution is fresh, has no assurance that all the carbon

dioxide has been absorbed; to be certain he must pass the gas into the caustic pipette once more and note whether the volume remains constant. Any further contractions must be added to the first. If more than five passes are required to get complete absorption, the solution should be discarded and a fresh one put in the pipette.

$$\text{Percentage of CO}_2 = \frac{\text{contraction} \times 100}{\text{c. c. of sample taken}}$$

UNSATURATED HYDROCARBONS OR ILLUMINANTS

Pass the gas six times into the fuming sulphuric acid pipette *q*, then remove the SO₃ fumes by passing the gas into the caustic pipette *p*; return the gas to the burette and read the contraction as prescribed under determination for carbon dioxide.

$$\text{Percentage of illuminants} = \frac{\text{contraction} \times 100}{\text{c. c. of sample taken}}$$

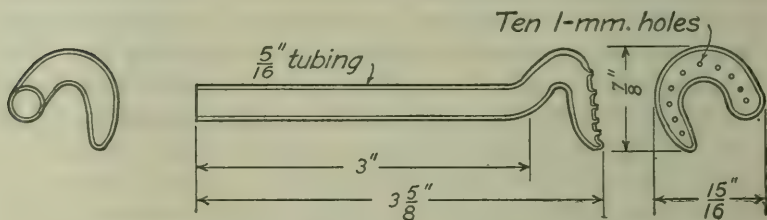


FIGURE 17.—Blower for combustion pipette

OXYGEN

Pass the gas into the pyrogallate pipette *r* six times for low oxygen content and fresh reagent, and twelve times for high-oxygen gases. If the volume does not remain constant after 12 passes, the solution should be renewed.

$$\text{Percentage of oxygen} = \frac{\text{contraction} \times 100}{\text{c. c. of sample taken}}$$

CARBON MONOXIDE AND HYDROGEN

Turn stopcocks *j*, *k*, and *n'''* to establish communication between the burette and combustion pipette *t* through the copper oxide tube *i*; lower the furnace *l* over the copper oxide tube and adjust the rheostat to give a temperature of 290° to 310° C.; pass the gas slowly (10 c. c. per minute) through the copper oxide tube into pipette *t* and back again into the burette at the same rate; repeat.

Raise the furnace and cool the copper oxide tube by directing a stream of compressed air from a blower tube, shown in Figure 17.

This tube consists of a piece of glass tubing closed at the end and bent into a one-turn coil with a number of small holes in one side of the coil. The open end is connected to one end of a compressed-air line or other source of air supply and is used for cooling the copper oxide tube and the combustion pipette by changing from one to the other as needed. Three minutes is enough for bringing the copper oxide tube back to room temperature. Return the gas to the burette and measure the contraction.

$$\text{Percentage of hydrogen} = \frac{\text{contraction} \times 100}{\text{c. c. of sample taken}}$$

Pass the gas into caustic pipette *p* several times to remove the carbon dioxide formed by combustion of the carbon monoxide, and then pass the gas through the copper oxide tube into pipette *t* to obtain the carbon dioxide remaining in the tube, and again pass it into the caustic pipette. Return the gas to the burette and measure the contraction.

$$\text{Percentage of carbon monoxide} = \frac{\text{contraction} \times 100}{\text{c. c. of sample taken}}$$

METHANE AND ETHANE

Store the residual gas in caustic pipette *p*, close cock *n*, and draw an excess of oxygen into the burette by way of cocks *b*, *c*, and *d*, connecting the oxygen supply at *w*. This supply may be from an "Oxone generator" or a tank of compressed oxygen; or, if the residual gas is low in combustibles, air may be used; 1 c. c. of methane requires 2 c. c. of oxygen or 9.56 c. c. of air, and 1 c. c. of ethane requires 3.5 c. c. of oxygen or 16.72 c. c. of air for complete combustion.

Measure the oxygen or air accurately and pass it into combustion pipette *t*, withdraw the residual gas from the caustic pipette into the burette, bringing platinum spiral *s* to bright-yellow heat by closing switch *u* and adjusting the resistance, and slowly pass the gas (10 c. c. per minute) into the combustion pipette, using all the residual gas. The rate of passing the gas can be conveniently regulated with a screw clamp on the rubber tube of the leveling bulb. When all the gas has passed out of the burette, open the screw clamp and pass the gas back and forth over the hot platinum spiral several times, and once through the copper oxide tube to sweep out the methane and ethane remaining in it. Keep the pipette cool with an air blast from the blower tube. Turn off the current, cool the pipette, and then return the gas to the burette. Measure and record the contraction as usual.

Pass the gas into the caustic pipette several times to absorb the carbon dioxide formed and again measure the contraction. To check

the completeness of combustion and remove the residual carbon dioxide left in the manifold, pass the gas once more into combustion pipette *t*, but quickly, because now an explosive mixture will be absent. Raise the platinum wire to the desired temperature and burn the gas again by passing it two or three times over this wire, cool the pipette, withdraw the gas into the burette, and measure the contraction as usual. If the first combustion is properly carried out, the contraction should be less than 0.2 c. c. Then absorb the carbon dioxide produced by passing into the caustic pipette and measure the contraction. Add the two contractions on burning and carbon dioxide values, and calculate the percentage of methane and ethane by the following equations:

$$\text{Percentage of ethane} = \frac{(2 \times \text{carbon dioxide formed} - \text{contraction}) \times 100}{1.5 \times \text{c. c. of sample taken}}$$

$$\text{Percentage of methane} = \frac{(\text{carbon dioxide formed} - 2 \times \text{ethane}) \times 100}{\text{c. c. of sample taken}}$$

Following is the result of a typical Orsat analysis:

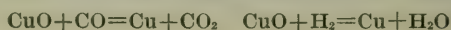
Typical Orsat analysis

Stages of analysis	Burette reading	Difference	Per cent
Volume of sample taken.....	47.85		
Carbon dioxide.....	46.55	1.30	2.7
Illuminants.....	44.70	1.85	3.9
Oxygen.....	44.45	.25	.5
Hydrogen by CuO.....	21.80	22.65	47.3
Carbon monoxide.....	19.20	2.60	5.4
Oxygen (or air) added.....	53.80		
Total volume.....	73.00		
Volume after combustion.....	36.25	36.75	
Volume after CO ₂ absorption.....	16.75	19.50	
Volume after second combustion.....	16.25	.50	
Volume after second CO ₂ absorption.....	15.40	.85	
Total contraction.....		37.25	
Total CO ₂		20.35	
Ethane = $\frac{2 \times \text{CO}_2 - \text{contraction}}{1.5}$		2.30	4.8
Methane (CO ₂ - 2 × ethane).....		15.75	32.9
Nitrogen (by difference).....			2.5

NOTES ON OPERATION OF APPARATUS

A complete analysis by the above method takes about 1 hour; at least a third of this time is required for determining the carbon monoxide and hydrogen.

The copper oxide tube supplying the oxygen for combustion must be cooled before the paraffin hydrocarbons are burned, as those remaining in the U tube are swept out either with oxygen or air. In the reduction of the copper oxide, which occurs when carbon monoxide or hydrogen is oxidized, the oxide is reduced thus:



If oxygen is passed through the tube while hot, some combines with the reduced copper to form CuO , thus giving too large a value for the contraction. If the available space in the copper oxide U tube is known, the air or oxygen used for combustion may be passed

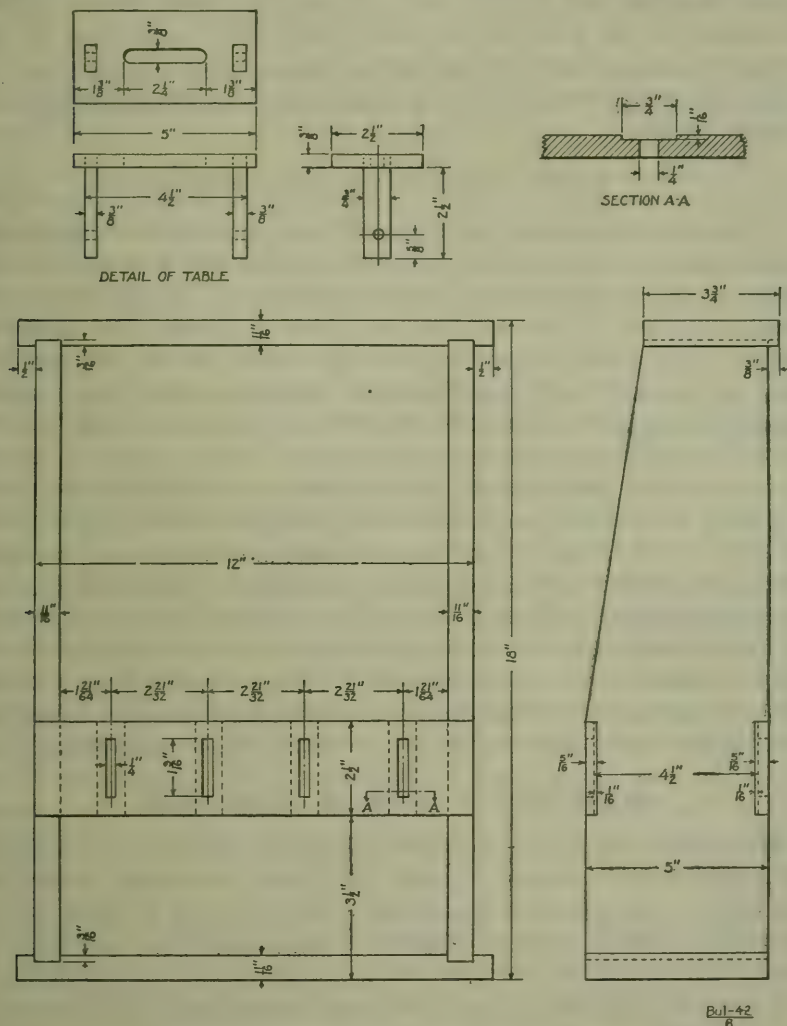


FIGURE 18.—Wooden support for Orsat apparatus

directly into the slow-combustion pipette without passing through the copper oxide tube and a correction applied for the amount of methane and ethane remaining in the tube. The time of analysis may be reduced to about 40 minutes, as it is unnecessary to cool the copper oxide tube after each combustion of the carbon monoxide and hydrogen. If this method is used, the furnace should be left in

place around the copper oxide before and throughout the analysis and maintained at a constant temperature.

In the preparation of the copper oxide tube, particles of metallic copper should be added to the copper oxide to serve as a catalytic agent when the tube is first used. Unless these particles are added the action of the first few samples is very slow until some of the copper oxide is reduced to the metal; then action is rapid.

The Orsat apparatus should be supported on a wooden fixture, as Figure 18 shows.

USE OF WATER IN BURETTE AND COMBUSTION PIPETTE

When a large number of analyses are being performed, as at plants where blast-furnace, producer, or illuminating gas is manufactured, water is usually substituted for mercury in a gas burette or a combustion pipette. Water may be used without the sacrifice of much accuracy if readings are taken promptly, and if several analyses are made earlier to saturate the water with carbon dioxide. As a further precaution against absorption of carbon dioxide the water should be acidified slightly with sulphuric acid.

An auxiliary compensating tube inclosed in the water jacket surrounding the burette compensates for changes of temperature and pressure in the Orsat apparatus described, so that any such changes during the analysis affect the gas in the burette and the air in the tube to the same extent. During the analysis the readings are all made by making connection to the compensating tube and bringing a mercury manometer to a certain mark. This method eliminates the effect of change of temperature and pressure during the analysis, and is more fully discussed under operation of the apparatus.

SOLUBILITY OF GASES IN ABSORBENTS

The errors caused by change of water-vapor content and solubility of gases in the confining liquid have been discussed under the operation of the Haldane apparatus. The solubility of gases in absorbents, however, requires further discussion. The precision to which an analysis can be carried is limited by the absorbents that are available for removing the different constituents. Not only do some absorbents remove chemically the constituents desired to be removed, but also there is a physical solution of some of the other constituents in the absorbents. The physical solubility of the simple gases, such as carbon monoxide, hydrogen, oxygen, nitrogen, and methane, is small, and when two or more analyses are made after fresh solutions have been put into the pipettes the error due to the solubility of the gases mentioned is very slight. Fuming sulphuric acid and bromine solution, used for the removal of unsaturated

hydrocarbons, and cuprous chloride solution, used in some apparatus for the removal of carbon monoxide, are the greatest offenders in this respect.

SOLUBILITY OF METHANE AND ETHANE IN FUMING SULPHURIC ACID AND CUPROUS CHLORIDE SOLUTION

Pure methane and ethane were prepared by the method of Gladstone and Tribe²² and passed into pipettes containing fuming sulphuric acid and cuprous chloride solution, with the following results:

No contraction in volume occurred when 100 c. c. of methane remained in contact with the acid 5 minutes. The gas was passed back and forth several times between the pipette and burette. No measurable contraction in volume occurred under the same conditions when the gas was brought in contact with the cuprous chloride solution.

When 100 c. c. of ethane was passed back and forth into fuming sulphuric acid for 2 minutes, it lost 1 per cent of its volume. At the end of 5 minutes a contraction of 2 per cent had taken place. When the same amount of ethane was passed back and forth into the cuprous chloride solution for 2 minutes, it lost 0.6 per cent of its volume, and at the end of 5 minutes the contraction was 1.4 per cent.

R. A. Worstall²³ determined that the paraffin hydrocarbons are soluble to a certain extent in fuming sulphuric acid, the higher members more so than the lower. He says that in examining a gas mixture containing members of the paraffin series of hydrocarbons, the use of fuming sulphuric acid to determine unsaturated hydrocarbons leads to no error if paraffins higher than ethane are absent, and if the gas mixture is in contact with the acid not longer than 15 minutes. Worstall's determinations were carried out by leaving the gas quietly in contact with the acid and having no increased absorption surface, such as is provided by the use of glass rods or beads.

Orndorf and Young²⁴ found that propane is slowly soluble in fuming sulphuric acid. Phillips²⁵ states that the higher members of the paraffin series are somewhat soluble in bromine water and in cuprous chloride solution. It follows, then, that if a natural-gas

²² Gladstone, T. H., and Tribe, Alfred, Notes on the preparation of marsh gas: Jour. Chem. Soc., vol. 45, 1884, p. 154. It was found that unsaturated hydrocarbons are produced in the preparation of methane by this method. They were removed by means of fuming sulphuric acid. F. G. Phillips, of the University of Pittsburgh, in conversation with the authors, reported a similar experience.

²³ Worstall, R. A., The absorption of methane and ethane by fuming sulphuric acid: Jour. Am. Chem. Soc., vol. 21, 1899, p. 145.

²⁴ Orndorf, W. R., and Young, S. W., The products of the condensation of acetone with concentrated sulphuric acid: Am. Chem. Jour., vol. 15, 1893, p. 249.

²⁵ Phillips, F. C., Oil and gas levels: West Virginia Geol. Survey, vol. 1A, 1904, p. 522.

mixture or other mixture containing higher paraffins is being examined and undergoes a reduction in volume when treated with the above reagents other tests should be performed to verify the presence of olefin hydrocarbons or of carbon monoxide. Qualitative tests of the use of palladium chloride²⁶ and blood solutions and quantitative tests by the iodine pentoxide method can be performed for such verification.

ACTION OF FUMING SULPHURIC ACID ON PITTSBURGH NATURAL GAS

According to combustion analyses performed at the bureau's laboratory, the natural gas used in Pittsburgh contains about 83 per cent methane and 16 per cent ethane. This 99 per cent of paraffins includes some propane and possibly some butane. When 100 c. c. of the gas was treated with fuming sulphuric acid and a cuprous chloride solution the following results were obtained:

Action of fuming sulphuric acid on the natural gas used in Pittsburgh

Number of passages of gas into pipette	Reduction in volume, per cent
3 -----	0.4
6 -----	.7
12 -----	1.4

Action of cuprous chloride on the natural gas used in Pittsburgh

Number of passages of gas into pipette	Reduction in volume, per cent
3 -----	0.5
6 -----	.6

The action of fuming sulphuric acid on a natural gas rich in the higher paraffins is shown below. The gas contained about 23 per cent ethane, 76 per cent propane, and 1 per cent nitrogen, and is used for the production of gasoline.

Action of fuming sulphuric acid on a natural gas rich in the higher paraffin hydrocarbons

Number of passages of gas into pipette	Reduction in volume, per cent
3 -----	5
6 -----	12.5
12 -----	14.5

The authors have also determined that bromine water has an appreciable solvent action on the higher paraffin hydrocarbons.

ELIMINATION OF ERRORS DUE TO PHYSICAL ABSORPTION

Most errors due to physical absorption are eliminated after several analyses of the same general composition have been made, because

²⁶ Phillips, F. C., Researches upon the phenomena of oxidation and chemical properties of gases: Am. Chem. Jour., vol. 16, 1894, p. 267.

the solutions become saturated with the different gases. When fresh solutions are put into the apparatus at least two analyses should be made before results are accepted as correct.

GRADUATION OF THE BURETTE

Accurate results can not be obtained unless the burette is properly calibrated. Makers of burettes usually calibrate them with fair accuracy, but it is difficult to obtain a uniform bore throughout the entire length, consequently a check calibration should be made. To make it, proceed as follows: Place the burette in a water jacket in the same positions as used and keep the temperature of the water as constant as possible. Seal a three-way stopcock to the lower end of the burette and attach a leveling bottle to one projection of the stopcock, so that if by accident the mercury is allowed to fall below a certain graduation mark on the burette during the calibrating operation the leveling bottle can be raised and the mercury easily brought back to the mark for calibration. Weigh successive 5-c. c. portions of mercury; calculate the volume of mercury at the observed temperature from the weight.

CAPILLARY ERROR OF THE APPARATUS

The apparatus is so constructed that the gas can be passed to the different pipettes without connecting or disconnecting any parts. The glass manifold and the connections leading to the cocks above the absorption pipettes through which the gas is distributed during an analysis contain about 3 c. c. of space. If this space contains an inert gas (nitrogen) before and after the analysis the error is largely overcome. Most of the capillary error is eliminated by sweeping out the manifold with nitrogen after each analysis. However, there is a small error because some of the gas is left below each stopcock above the absorbents. To minimize this error, the distance between the cocks and surface of the absorbents is made as small as possible, and small capillary tubing is used for the connections. If the gases being analyzed do not differ appreciably in composition, the capillary error largely compensates itself; that is, the gases introduced into the capillaries and removed have about the same composition, and the gases gained and lost in the capillaries as the analysis progresses are relatively the same.

FORMATION OF OXIDES OF NITROGEN

Are oxides of nitrogen ²⁷ formed during the combustion analysis? Gas analysts have raised this question as affecting the accuracy of their

²⁷ White, A. H., The oxidation of nitrogen as a source of error in the estimation of hydrogen and methane: Jour. Am. Chem. Soc., vol. 23, 1901, p. 476.

work. White says that neither the explosion method nor any other involving active combustion can give strictly accurate results. Jones and Parker,²⁸ using the phenyl-disulphonic acid method whereby quantities of oxides of nitrogen as low as 0.001 c. c. could be detected, found that the production of oxides of nitrogen by the slow-combustion method when the time of burning was not more than 3 minutes and the wire not heated beyond a bright yellow, was within the experimental error of routine gas analysis. Under the above conditions not more than 0.003 c. c. of oxides of nitrogen was produced. The purity of the platinum wire had no effect on the production of oxides of nitrogen. None was produced by the explosion method when air was used as the oxygen supply, but when mixtures of air and oxygen were used as the oxygen supply, appreciable quantities of oxides of nitrogen were formed, too large to be disregarded in gas analysis. The production of oxides of nitrogen by the explosion method is due to the flame temperature developed by the gas mixture when exploded rather than to the sparking across the electrodes. The addition of oxygen raises the flame temperature, which reaches a critical point above which appreciable quantities of oxides of nitrogen are produced.

DISTILLATION OF MERCURY

Apparatus for the distillation of mercury, devised by G. A. Hulett,²⁹ former chief chemist of the Bureau of Mines, are used by the authors. His description of the apparatus is given below. The mercury is first filtered through chamois skin, then dropped in a fine stream through diluted nitric acid, and distilled in retorts heated by gas or electricity. Air is passed through the vapors to oxidize any volatile metals carried over in the distillate.

DESCRIPTION OF MERCURY STILL

Figure 19 gives an idea of the essential details of the gas-heated retort; *g* is a common asbestos air bath with a hole in the bottom for the flame; above is fastened a shallow metal cup that supports the flask and on which the flame plays. The flask *a* is of the ordinary round-bottom type holding 250 to 500 c. c. The neck is drawn down short, and the 20-cm. tube *b* sealed on, as is also the thin-walled side tube *e*, which is 10 to 15 mm. in diameter and 50 cm. long; *e* serves as the air-cooled condenser. A tube, *c*, is selected of such a diameter that it will snugly fit the tube *b*; to it is sealed a glass cock, and the

²⁸ Jones, G. W., and Parker, W. L., The formation of oxides of nitrogen in the slow-combustion and explosion methods in gas analysis: Jour. Ind. Eng. Chem., vol. 13, 1921, p. 1154.

²⁹ Hulett, G. A., The distillation of amalgams and the purification of mercury: Phys. Rev., vol. 34, 1911, p. 307.

tube is drawn out fine at the lower end. This tube is slipped into the tube *b* as indicated in the figure. The joint *d*, where there is a slight enlargement of the tube *c*, is made tight with rubber bands about 1 cm. wide, which are wrapped about the joint while stretched. The asbestos shields *s* deflect the hot gases so that this joint never gets warm, even to the hand. The joint is much simpler than a ground joint, which may be used.

The glass cock regulates the rate at which the air bubbles through the mercury in the still, and if it is properly ground no grease need be used on it. The end of the condensing tube *e* is sealed to the stopper of an ordinary Drexel washing bottle. The outlet tube from the Drexel bottle *f* is joined to an ordinary Sprengel suction

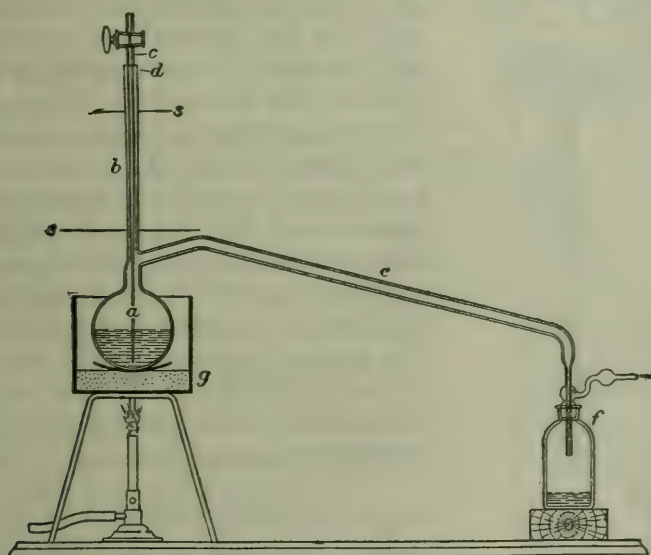


FIGURE 19.—Gas-heated mercury still. For explanation, see text

pump and a manometer, and a vacuum of 25 to 30 mm. is maintained in the system while air is bubbling through the mercury in the still. When the still is once uniformly in operation it needs little attention, and 2 kg. of mercury may be distilled in 2 or 3 hours. Steady gas and water pressures are desirable. The ground joints may readily be made tight enough by a little grinding with fine emery, if they are not satisfactory at the start. The rubber joint at *d* never gives trouble if the tube fits well in the neck of the flask.

DESCRIPTION OF STILL WITH ELECTRIC HEATER

In distilling large amounts of mercury it has been found necessary to use a larger still provided with an electric heater and so arranged

that mercury can be introduced during distillation. Figure 20 presents the main features of the still. The flask *a* is about 15 cm. in diameter, and into the bottom is sealed the glass tube *g* which connects with the reservoir *h*. The cock *g* is ordinarily left open. It was found that the air might be admitted from below through the side tube *s* instead of from above through the neck, as in the still of Figure 19. At *f* is a ground-glass joint. The inserted tube ends in a capillary which delivers the air well into the tube *g*, where it bubbles up through the mercury and into the still. With this

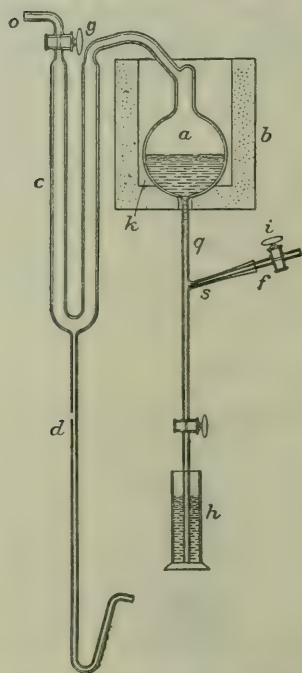


FIGURE 20.—Electrically heated mercury still. For explanation, see text

arrangement the rate at which the air is passing into the mercury can always be observed and controlled with the cock *i*. Mercury is allowed to flow into the reservoir *h* at any desired rate and thus the rate at which it enters the flask is controlled. The mercury vapor is condensed in the large U tube *c*, which is made from 25-mm. thin-walled tubing and is 50 cm. long, thus giving a condensing tube 1 meter long. The tube *c* is joined to a Sprengel suction pump and manometer, and a vacuum of 25 to 30 mm. is maintained in the apparatus during distillation. The mercury condenses in the tube *c* and collects in the tube *d* and flows out at the bent-up end. This tube *d* is about 1 meter long and 4 mm. in diameter.

ELECTRIC HEATER

The electric heater *b* is made of asbestos, water glass, and magnesium oxide cement, with heating coils of nichrome ribbon on the sides and bottom. The bottom part of the still is made from strips of asbestos 40 mm. wide and 1.5 mm. thick. The nichrome ribbon is placed along the edge of these strips, and then they are rolled up together, forming the ribbon into a spiral very close to one side of the "wheel" thus fabricated. The asbestos strips are well wet with water and the mixture of water glass and magnesium oxide, and after they are wound may, while still wet, be dished to fit the bottom of the flask. Thus the flask has a good support and the heating coil is at a place where it will be most effective. A short piece of brass tubing is attached to the end of the nichrome ribbon as a conveni-

ence in starting the roll. This brass tube serves as a hole for the tube *g*, and also as one terminal for the heating coil. For 110-volt circuits this coil should have a resistance of 12 to 15 ohms.

A thin piece of asbestos is wound on a cylindrical form of the desired diameter. The asbestos wheel just made is forced into one end of the cylinder, and on its outside is wound nichrome ribbon to form the heater for the sides. A resistance of about 5 or 6 ohms is needed here. Around the cylinder is wound a layer of asbestos wet with the cement, and over all are wound several layers of asbestos for insulation. The top of the heater is also covered with asbestos and glass wool. More resistance will be needed if all the heat from the 110-volt circuit is to be used in the heater, and a spiral of nichrome wire may be placed in the lower inside corner of heater *k*. The resistance of this coil may be adjusted so that no external resistance need be used. Normally the rate of distillation should be such that the mercury vapor is condensing over nearly the whole length of the condenser.

The apparatus is fastened to an upright support which is part of a large tray; a bracket holds the heater.

CARE OF APPARATUS

After the still is used, run out the last of the mercury and draw an acid up into the flask *a*, and the condensing tube if necessary (1:1 nitric acid is best for this purpose); after the acid, use distilled water. The still is easily cleaned and dried without dismantling. The glass cocks should be well ground to avoid the use of grease or organic matter, but the cocks need not be perfectly tight. Draw air through the mercury at the rate of about 5 c. c. per minute.

LABORATORY CONTAINER FOR HOLDING GASES OVER MERCURY

Figure 21 shows a container, which requires only a small amount of mercury, for holding gases that have been prepared in the laboratory. It follows the principle of one devised by Hempel,³⁰ and is also similar in construction to Travers's,³¹ except that a three-way

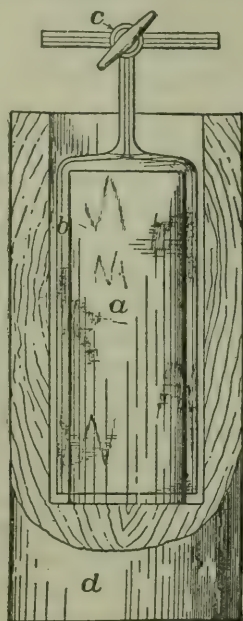


FIGURE 21.—Container for gases. For description, see text

³⁰ Hempel, Walther, *Methods of gas analysis*. 3d German ed., trans. by L. M. Dennis, 1910, p. 29.

³¹ Travers, M. W., *The experimental study of gases*. 1901, p. 30.

stopcock has been sealed at the stop instead of the two-way cock which they used.

Remove cylindrical core from the block of hardwood *d* and cement a smaller cylindrical core, *a*, in place, as shown; the gas holder *b*

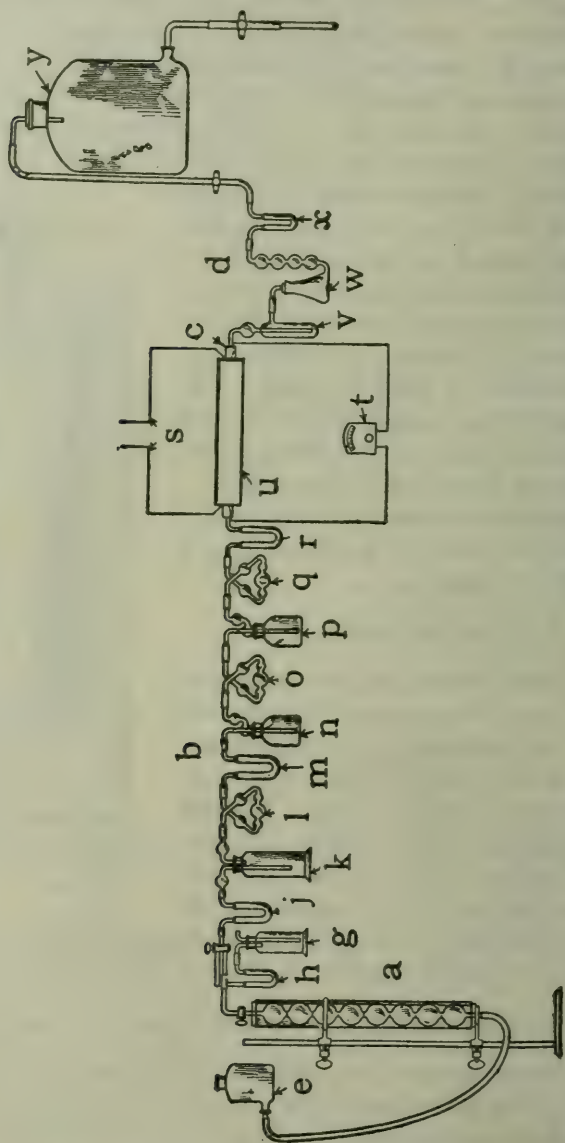


FIGURE 22.—Apparatus for determination of carbon monoxide by means of iodine pentoxide. For explanation, see text

fits closely over the inner cylinder. In using the instrument, first draw the mercury up into the stopcock. On account of the buoyancy of the glass exert pressure to expel the gas. First turn the three-way stopcock so that gas, as it is prepared, is passed through the

stopcock and into the air until all connections are thoroughly swept out with the pure gas; then turn it so that the stream is directed into the gas holder. The buoyancy of the glass causes the cylinder to rise as the gas enters.

SIMPLIFIED APPARATUS FOR DETERMINING CARBON MONOXIDE

In the apparatus shown in Figure 22 the authors have introduced two features which simplify the work of determining the amount of CO in a gas sample, an electrically heated wire-wound jacket for holding the iodine pentoxide tube and a bulb burette for measuring the sample. The tube is heated quickly. A temperature of 150°C . is satisfactory. Experiments by the authors indicate, but do not prove, that lower temperatures will suffice. The bulb burette consists of eight 100-c. c. bulbs. A narrow graduated constriction joins each bulb with the next, so that measurements can be accurately made at atmospheric pressure by means of the leveling bottle. Any number of bulbs up to eight can be used for measuring the sample.

The CO_2 produced is absorbed by a standard solution of barium hydroxide, and the excess is titrated with an oxalic acid solution containing 0.56325 gram per liter; 1 c. c. of barium hydroxide should equal 1 c. c. of the oxalic acid solution, and 1 c. c. of this oxalic acid solution equals 0.10 c. c. of CO at 0°C . and 760 mm. pressure.

A prepared mixture of CO and air containing 0.04 per cent of CO, as determined by a combustion analysis with the apparatus shown in Plate III, when analyzed by the iodine pentoxide method with 800 c. c. of sample, showed a CO content of 0.043, 0.043, and 0.043 per cent. The train illustrated in Figure 22 has proved ample to remove H_2S , SO_2 , CO_2 , and unsaturated hydrocarbons from the gas sample before it enters the iodine pentoxide tube. Mixtures of illuminating gas and air, prepared to contain CO in known proportion, have been passed over the iodine pentoxide tube and the correct proportion of CO determined.

DESCRIPTION OF APPARATUS

The apparatus shown in Figure 22 consists in general of the bulb burette *a*, the purifying train *b*, the iodine pentoxide tube *c*, and the collection train *d*; *e* is a leveling bottle, and *j* a U tube containing pumice stone and sulphuric acid; *k* contains a lead acetate solution for retaining H_2S if present, *l* contains a standard solution of barium hydrate for retaining any CO_2 in the sample, *m* contains pumice stone and sulphuric acid, *n* fuming sulphuric acid, *o* concentrated sulphuric acid, *p* a KOH solution, *q* and *r* concentrated sulphuric acid; *s* designates the furnace leads; *u* is a wire-wound elec-

tric furnace for holding the iodine pentoxide tube; *v* contains a KI solution for retaining iodine; *w* is a standard solution of barium hydroxide for absorbing CO_2 produced by the reaction between the iodine pentoxide and CO; *x* is a guard tube containing soda lime; *v* is an aspirator bottle; and *t* is a galvanometer connected to a constantan-copper thermocouple. The thermocouple in a porcelain tube is placed inside the iodine pentoxide tube to register the temperature.

The purifying train through which the air is passed to sweep out the train after an experiment embraces *g*, containing a potassium hydroxide solution, and *h*, containing soda lime.

The authors have found that the iodine pentoxide must be purified by passing air at a temperature of 200°C . over it for several hours before determinations are made.

Later experiments performed by the authors indicate that in the afterdamp of mine explosions, in air vitiated by the firing of explosives in mines, or in air vitiated by the exhaust from gasoline locomotives, gases other than CO that reduce iodine pentoxide are seldom present in large enough quantity to necessitate the use of the long purifying trains shown in the illustration. This statement refers to mixtures in which the CO is present in proportions under 0.2 per cent. In other words, the amount of other products of incomplete combustion that reduce the iodine pentoxide in the atmospheres mentioned is very much less than the amount of CO.

One column of the following table gives the CO as found by combustion analyses with the apparatus shown in Plate III. Methane and hydrogen were also present, and were determined with the CO by burning all three gases together. Another column gives the CO for the same sample, as determined by the iodine pentoxide method:

Results of two methods of analysis to determine carbon monoxide in gas samples

Sample No.	Method of analysis		Sample No.	Method of analysis	
	Combustion	Iodine pentoxide		Combustion	Iodine pentoxide
	<i>Per cent</i>	<i>Per cent</i>		<i>Per cent</i>	<i>Per cent</i>
1.....	0.06	0.072	4.....	0.11	0.120
2.....	.10	.095	5.....	.07	.073
3.....	.10	.082	6.....	.02	.020

In making the above analyses by the iodine pentoxide method 400 c. c. of sample was used. The purifying train consisted of four washing bottles; two contained concentrated sulphuric acid and the other two potassium hydroxide solution. One determination required about $2\frac{1}{2}$ hours.

IODINE PENTOXIDE APPARATUS USING LIQUID AIR

More recent tests by Teague³² in connection with the investigation of the physiological effects of motor exhaust gas showed that the above method was subject to error if gasoline vapor or other heavy unsaturated-hydrocarbon vapors were present. These impurities, however, seldom exist in mine atmospheres, but when they do Teague found it necessary to purify the gases before they reached the iodine

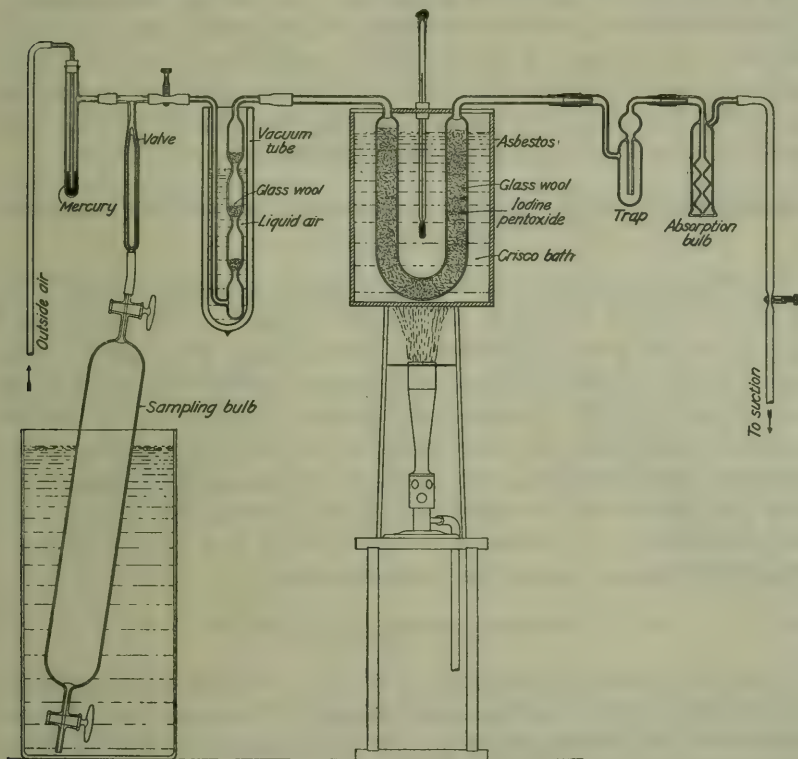


FIGURE 23.—Iodine pentoxide apparatus for determination of carbon monoxide, using liquid air to remove impurities

pentoxide tube by passing them through a bath containing liquid air. Figure 23 shows a diagram of the apparatus. The iodine pentoxide tube was made of three-fourths-inch pyrex tubing 10 inches long and was filled with alternate layers of glass wool and iodine pentoxide, totaling 30 to 40 grams. The arm of the exit side of the U tube was somewhat longer than the other and tapered to make an interlock glass joint with the guard tube. A similar joint was made with the absorption bulb, thus removing the possibility of

³² Teague, M. C., The determination of carbon monoxide in air contaminated with motor exhaust gas: Jour. Ind. Eng. Chem., vol. 12, 1920, p. 964

error due to rubber connections. To condition the iodine pentoxide, raise the temperature of the bath from 220° to 230° C. for several hours, while air is drawn through. Iodine pentoxide prepared by the chloric acid (HClO_3) method proves more suitable and gives lower blanks than that made by the oxidation of iodine with fuming nitric acid. Barium hydroxide solutions much weaker than 0.02 N have proved undesirable, whereas 0.001 N thiosulphate could be used in the determination of the iodine liberated by the reaction, a difference which offsets the advantage of the greater amount of CO_2 formed. By the use of the liquid-air bath all of the CO_2 , water vapor, unsaturated-hydrocarbon vapors, and gasoline vapors are removed from the sample being analyzed, thus eliminating the long purifying train necessary with the apparatus described before.

DETERMINATION OF CARBON MONOXIDE BY THE PYROTANNIC ACID METHOD

The Bureau of Mines has recently developed a new method³³ for the determination of CO in air which is based on the fact that a light brownish gray suspension is formed in a few minutes when normal blood, diluted with water, is treated with a solution of tannic and pyrogallic acids, whereas light carmine suspensions are formed in blood having CO in combination with the hæmoglobin. When compared with standards the intensity of the carmine suspension gives the percentage of saturation of the hæmoglobin in the blood used for testing. By means of suitable curves (fig. 24) the percentage of CO in the air tested can be determined.

APPARATUS NECESSARY FOR TEST

1. Set of permanent standards (Pl. VI, p. 43), made to match the color of blood having varying amounts of CO-hæmoglobin (0, 10, 20, 30 per cent, etc.), arranged in a rack with spaces between for interposing tubes of similar size containing specimens of blood for analysis.
2. Small test tubes (of the same size and glass as those used for standards) for preparing specimens of blood.
3. A dilution pipette for measuring blood. The long capillary stem is calibrated to a 0.10-c. c. mark, and the total pipette has a volume of 2 c. c., or a ratio of 1 to 20.
4. A spring hæmospast for making small puncture wounds from which the blood is obtained.

³³ Sayers, R. R., Yant, W. P., and Jones, G. W., The pyrotannic acid method for the quantitative determination of carbon monoxide in blood and air: Repts. of Investigations. Serial No. 2486, Bureau of Mines, June, 1923. 6 pp.; Tech. Paper 373, Bureau of Mines, 1925, 18 pp.

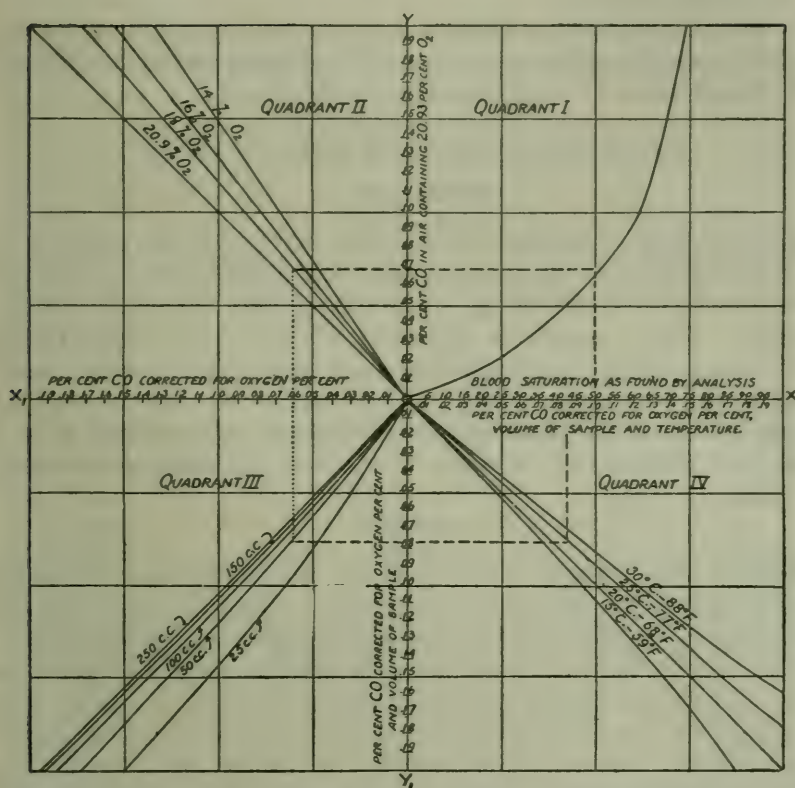


FIGURE 24.—Curves for calculating the percentage of carbon monoxide from the percentage of blood saturation

If the percentage of oxygen is between 19 and 20.9 per cent, the volume of the sample taken for analysis is 250 c. c. or greater, and the testing is made at temperatures between 63° and 73° F. (17°–23° C.); the CO values are read directly from quadrant I. Example: If percentage saturation is found to be 50 per cent, this value is taken on the OX axis, and the vertical line passing through this point is followed upward until it intercepts the curve, then horizontally to the left to the OY axis. The point of interception of the OY axis gives the CO (0.07 per cent).

If the sample contains less than 19 per cent oxygen, correction is made for reduced oxygen percentages by following the horizontal line through the OY axis into the second quadrant until it intercepts the curve representing the oxygen percentage which the sample contains. The vertical line passing through this point is followed down to where it intercepts the OX axis, the interception with which gives the corrected per cent of carbon monoxide (0.06 in the above example).

If the sample used is less than 250 c. c., the vertical line is extended into the third quadrant until it intercepts the curve representing the volume of the sample taken; then from this point the horizontal line is followed to the right until it intercepts the OY axis, and the corrected percentage of CO is read (0.077 per cent).

If the temperature is not between 63° and 73° F., the horizontal line is extended into the fourth quadrant until it intercepts the curve representing the temperature at which the analysis was made; then, from this point the vertical line upward is followed to the OX axis, the interception of which gives the corrected percentage of CO (0.085 per cent).

5. Rubber hose for wrapping around the finger during the taking of the blood sample.

6. Tannic-pyrogallic acid mixture (0.04 gm. of a 1:1 mixture), for producing the color suspension in the diluted specimen of blood.

7. Small bottle of water for diluting the blood.

PROCEDURE FOR TESTING FOR CARBON MONOXIDE

SAMPLING THE GAS

Use any type of narrow-mouth bottle for taking the samples to be tested; preferably the bottles should hold at least 200 c. c., and the neck should be small enough to be closed with a cork or rubber stopper. Take a sample by aspirating the gas to be tested into the bottle in a manner as described under sampling of mine gases. Squeeze the bulb at least fifty times to make sure that the original air in the bottle has been completely removed and replaced with a sample of the gas to be tested. Then close the bottle with a cork or rubber stopper.

ANALYSIS

Make a small puncture wound at the tip of the finger with the hæmospast. If the blood does not flow freely, wrap the finger with the rubber hose, beginning at the base and progressing toward the tip. When a large drop of blood appears, catch it in a spot plate or draw it directly into the dilution pipette to the 0.1-c. c. mark. Dip the tip of the pipette into the container of distilled water, and draw water into the pipette until the solution reaches the 2-c. c. mark, then force it into the bottle containing the sample of gas to be tested. Replace the stopper, and rotate the bottle constantly for 15 to 20 minutes, so that the blood will absorb the CO in the sample of gas. Pour the blood solution into a test tube, add a small portion of pyrotannic acid (an amount which will remain on the point of a penknife blade is enough), close the end of the test tube, and invert the tube three or four times to insure thorough mixing. Place the tube in the rack and let it stand 15 minutes at room temperature, then compare it with the standards by interposing it between them and finding the standard which it most nearly matches. The percentage of CO-hæmoglobin is estimated from the value of that standard. Make observations by daylight, if possible, but not in direct sunlight. Calculate the percentage of CO present from the curves shown in Figure 24.

CORRECTIONS

Be sure that the sample of gas is so large (200 c. c. or more) that the amount of CO absorbed by the blood solution does not materially

alter the percentage of CO in the sample, otherwise a correction must be made.

Temperature and percentage of oxygen in the air also affect the results, but corrections for these are seldom necessary. However, as shown in Figure 24, whenever the oxygen is not below 19 per cent and temperature is between 65° and 72° C., no corrections are necessary. If corrections for size of sample, reduction of oxygen percentage, and change of temperature are necessary, the correct percentage of CO from the saturation of the blood used in the test can be found directly from the curves in the other three quadrants of Figure 24. A typical example of the application of the curves is given at the bottom of this figure.

DETECTION OF CARBON MONOXIDE IN MINES

The Bureau of Mines has already called attention to the futility of attempting to detect CO in the mine by the ordinary test³⁴ with the flame safety lamp, but some persons still believe the contrary. The bureau has found that the cap or any other change in the flame of the safety lamp from the action of CO is not distinguishable from changes produced by methane (CH_4). It will be granted that the cap or other change produced by 1 per cent of CH_4 in the mine air can be seen only with difficulty when the ordinary testing flame is used. Such a proportion of CO is enough to cause unconsciousness in less than 5 minutes and death in 5 to 10 minutes. The bureau made detailed tests to determine the exact effect of CO and CH_4 on the flame of a lamp. Although chemical tests, such as a blood test or absorption of the CO in cuprous chloride solution in a gas-analysis apparatus, are reliable, in the authors' opinion the use of birds (canaries) is much superior in that a test is quickly made, requires no technical experience, and is exact enough. Mice were formerly used as well as birds, but it has been found, both in the mine and laboratory, that mice are unsuitable subjects and they are now rarely employed in the detection of carbon monoxide. The Bureau of Mines uses canaries only, in mines after explosions or after and during fires, and in the laboratory. Some observations as to their behavior follow:^{34a}

USE OF BIRDS IN MINES AND THE LABORATORY

Because mice may be slow in responding to the presence in mine air of such small percentages of CO as would cause distress to a man at work, experiments similar to those performed with mice were tried with birds. Canaries were confined in a bell jar in atmospheres containing the following percentages of CO: 0.09, 0.12, 0.15, 0.2, and 0.29 per cent.

³⁴ Burrell, G. A., The use of birds and mice for detecting carbon monoxide after mine fires and explosions: Tech. Paper 11, Bureau of Mines, 1912, 15 pp.

^{34a} Burrell, G. A. Work cited, pp. 10-11.

After an exposure of 1 hour to an atmosphere containing 0.09 per cent of CO, a bird was not affected to such an extent that it would, if carried into a mine, indicate by its actions the presence of that proportion of CO. Only by close observation could one detect that the bird at the end of an hour felt slightly distressed.

With 0.12 per cent of CO in the atmosphere of the bell jar a bird did not show clearly symptoms of being affected. In about 15 minutes it had lost its liveliness and thenceforth remained comparatively quiet. The bird did not fall from the perch, but close observation showed that it was decidedly weaker at the end of the hour than was the bird placed in air containing 0.09 per cent of carbon monoxide.

In air containing 0.15 per cent CO a bird evinced symptoms of slight distress in 3 minutes. It gasped, gradually became weaker, swayed, and at the end of 18 minutes fluttered from the perch. At the end of an hour it had not lost all muscular power, but showed symptoms of extreme weakness.

In air containing 0.2 per cent of CO a bird showed pronounced symptoms of distress in $1\frac{1}{2}$ minutes; it became very unsteady in 3 minutes and fell from the perch in 5 minutes. After it was taken from the jar it regained its feet in 2 minutes and appeared to be in normal condition in 5 minutes.

In air containing 0.29 per cent of CO a bird fell from the perch in $2\frac{1}{2}$ minutes. When placed in fresh air again it had almost revived in 5 minutes.

Canaries are good indicators of the presence of noxious gases in mine atmospheres, as they quickly show signs of distress when small quantities of CO are present. A bird sways noticeably on its perch before falling, and its fall is a better indication of danger than the squatting, extended posture some mice assume without struggles, attempts to walk, or other preliminary symptoms of poisoning. Consequently birds not only give more timely warning of the presence of small quantities of CO, but exhibit symptoms that are more easily noticed by exploration parties.

The Bureau of Mines has made an extensive series of tests, which show that after canaries and other small animals have apparently recovered from exposure to CO, they may be used repeatedly without losing their efficiency in detecting gas. In these tests the animals were subjected to the action of the gas until they collapsed and then were placed in fresh air. As far as the eye could see they recovered as quickly after they had been exposed many times as after the first time. In the presence of 0.25 per cent of CO, birds and mice collapsed much more quickly than men, but recovered much more quickly. Of all the small animals tested, the canaries seemed most suitable for use in mines.

DETERMINATION OF OXIDES OF NITROGEN IN MINE AIR

The authors have performed some experiments to determine the adaptability of Busch and Gutbier's nitron method³⁵ for the de-

³⁵ Gutbier, A. [The quantitative analysis of nitric acid and nitrates by means of "nitrons"]: *Ztschr. angew. Chem.*, Jahrg. 18, Mar. 31, 1905, p. 494. Busch, Max. [Oxidation of nitrous acid by hydrogen peroxide. Estimation of nitrates in the presence of nitrates]: *Ber. Deutsch. chem. Gesell.*, Jahrg. 39, March, 1906, pp. 1401-1403.

termination of small quantities of oxides of nitrogen in mine air. Blasting sometimes produces these oxides in harmful quantities. Any nitric oxide when first produced combines with oxygen to form red fumes consisting chiefly of nitric peroxide.

Nitron (diphenylendoanilodihydrotriazol) has the formula $C_{20}H_{16}N_4$. The nitrate of this base has the formula $C_{20}H_{16}N_4HNO_3$. According to Busch, nitron can be used qualitatively to determine 1 part of HNO_3 , or nitrate, in 60,000 or 80,000 parts of a solution.

The writers are indebted to C. G. Storm, former explosives chemist of the Bureau of Mines, for suggesting an adaptation of Busch and Gutbier's method for the estimation of small quantities of nitrous fumes in mine air. Before the authors made their experiments, Storm obtained satisfactory results in using this method for the analysis of a gas sample containing a large amount (11.1 per cent) of oxides of nitrogen. The sample represented the gases that resulted from burning a gelatin dynamite in an atmosphere deficient in oxygen.

NITRON METHOD

In the authors' experiments measured amounts of nitric oxide prepared in a Lunge nitrometer from pure nitrates were added to bottles filled with air, and the following procedure used by Storm was adopted for estimating the nitric oxide.

By means of a separatory funnel, 10 c. c. of a 5 per cent solution of potassium hydroxide and 10 c. c. of a 3 per cent solution of hydrogen peroxide were poured into each bottle, the hydrogen peroxide to oxidize the nitrous fumes to nitric acid, and the potassium hydroxide to form potassium nitrate. The bottles were shaken frequently to insure complete oxidation and absorption. Next the solutions were washed into 200-c. c. beakers, wash water being used sparingly so that the total volume of solution was not greater than 30 or 40 c. c.. The solutions were then made slightly acid with 10 per cent sulphuric acid solution, a few drops of which at a time were allowed to flow down the sides of the beaker; finally 0.5 c. c. of acid was added in excess of that required for neutralization. These solutions were heated to boiling, and an excess of nitron solution (10 per cent by weight of nitron in a 5 per cent solution of acetic acid) was added. Theoretically, 1 c. c. of nitric oxide requires 0.01344 gram of nitron, or 0.1344 c. c. of a 10 per cent nitron solution. Then the burners were removed and the solutions allowed to cool to room temperature. Frequent stirring of the solutions during cooling hastened the precipitation of the nitron nitrate. After cooling, the beakers were put in an ice bath for about 2 hours, when precipitation was complete.

The nitrate usually appeared as long, fine needles, but when the larger amounts of nitrate were present it had much the appearance

of fine particles of asbestos. When concentration of the solution was carried too far before precipitation, the solution became semisolid, but this condition did not interfere with the formation of the precipitate. When 3 or 4 c. c. of ice water was added and the mixture shaken, the solution again liquefied, the nitron nitrate only remaining as a precipitate. Satisfactory results were not obtained with four samples whose volume of solution was much more than 30 or 40 c. c. before the addition of nitron solution. The precipitates of nitron nitrate in ice-cold solution were decanted into a weighed Gooch crucible with an asbestos mat and subjected to slight suction. The filtrates were used to wash the precipitates from the beakers. After the precipitates had been completely transferred to the filter, they were washed with four or five successive small portions of ice water, about 2 c. c. to a portion, and the precipitate was allowed to suck dry after each addition of ice water. The Gooch crucibles were then dried at 105° C. to constant weight.

The authors obtained the following results when they followed closely the procedure described above:

Results of gas analysis with the nitron method

Sample No.	NO present	NO found	Sample No.	NO present	NO found
	<i>C. c.</i>	<i>C. c.</i>		<i>C. c.</i>	<i>C. c.</i>
1-----	3.7	3.5	6-----	0.2	0.2
2-----	2.4	2.4	7-----	.2	.2
3-----	2.8	2.6	8-----	.8	.6
4-----	.9	.6	9-----	1.7	1.5
5-----	2.7	2.5			

These results show that with a large enough sample of mine air (5 to 10 liters) detection of quantities of nitric oxide much below that required to produce harmful effects on men is possible by this method.

To calculate the volume of nitric oxide corresponding to the weight of nitron nitrate, the following data are required:

Molecular weight of nitron, 312; molecular weight of nitron nitrate, 375; molecular weight of nitric oxide, 30; weight of 1 c. c. of nitric oxide, at 0°C. and 760 mm. pressure, 0.001341 gram; 0.001368 gram of nitron nitrate equals 1 c. c. NO.

PHENOL-DISULPHONIC ACID METHOD

PROCEDURE

The nitron method is not accurate enough for determining the very low percentage of oxides of nitrogen usually found in mine air; therefore, more sensitive methods were investigated. This study resulted in the development of the phenol-disulphonic acid method,³⁶

³⁶ Allison, V. C., Parker, W. L., and Jones, G. W., The determination of oxides of nitrogen: Tech. Paper 249, Bureau of Mines, 1921, 16 pp.

an application of the method used in water analysis for the determination of nitrates. The procedure is as follows: Shake samples of the gas to be tested with or bubble them through 10 per cent caustic soda or potash solution, then treat this solution for oxides of nitrogen as described later. In the Bureau of Mines gas laboratory the samples are received in vacuum-bulb containers. The neck of the bottle is scratched with a file and broken off, and the opening immediately closed with a cork stopper. Put 5 c.c. of 10 per cent caustic soda and 5 c.c. of hydrogen peroxide in the bottle and stopper it again. Rotate the bottle to coat the inside with the solution and then leave it for 30 minutes. Open the tube, wash the contents through a filter paper into a 150-c. c. beaker, and evaporate to dryness on a hot plate. During the evaporation cover the beaker with a watch glass to prevent contamination of nitrates from outside sources and to prevent loss of precipitate from spattering during the final drying period. Do this drying at a lower temperature to prevent the precipitate from caking. Moisten the residue with 2 c.c. of a 50-50 mixture of phenol-disulphonic acid and cold, concentrated sulphuric acid, dilute with 10 c. c. of distilled water, and run through a filter paper into a Nessler tube; rinse and wash as usual. Then add 15 c.c. of 11 to 1 strong ammonia and water; make up the whole to 100 c.c. and compare with color standards.

REAGENTS FOR DETERMINATION

PHENOL-DISULPHONIC ACID

Dissolve 25 grams of pure white phenol in 150 c. c. of concentrated sulphuric acid; add 75 c. c. of fuming sulphuric acid (15 per cent SO_3); stir well; and heat for 2 hours at 100°C .

STANDARD NITRATE SOLUTION

Make a solution of potassium nitrate containing 0.72 gram of KNO_3 per liter. Evaporate 10 c. c. of this solution on the water bath until about 1 drop is left, and remove the remaining water with a current of dry air. Quickly and thoroughly moisten the residue with 2 c. c. of the phenol-disulphonic acid solution, and make it up to 1 liter; 1 c. c. of this solution equals 0.001 mg. N_2 , or 0.00175 c. c. of NO_2 .

AMMONIA SOLUTION

Use equal parts of strong ammonia and distilled water.

CAUSTIC SODA SOLUTION

Prepare a 10 per cent, by weight, caustic soda solution, being sure that the caustic soda does not contain nitrates.

HYDROGEN PEROXIDE

Use standard commercial 3 per cent hydrogen peroxide free from acetanilide and nitrates.

Standards used for determining oxides of nitrogen are usually made up as follows:

Standards

Standard No.	Stand- ard nitrate solution	Oxides of nitrogen	Parts per million, based on 250 c. c. at 24° C. and 745 mm. Hg	Standard No.	Stand- ard nitrate solution	Oxides of nitrogen	Parts per million, based on 250 c. c. at 24° C. and 745 mm. Hg
	C. c.	C. c.			C. c.	C. c.	
1	0	0.00000	0	5	7	0.01225	49
2	1	.00175	7	6	10	.01755	70
3	2	.00350	14	7	15	.02625	105
4	4	.00700	28	8	20	.03550	140

The parts per million given in the table are based on a 250-c.c. sample, but by increasing the volume of sample taken the accuracy of the method can be increased accordingly, so that one or two parts per million can be obtained easily. Should the oxides of nitrogen be present in amounts which exceed the set of standards given, the solution should be diluted enough to come within the set of prepared standards and the results corrected for the amount of dilution. The hydrogen peroxide is added for the purpose of oxidizing any nitric oxide (NO) to nitrogen peroxide (NO₂).

USE OF THE GAS INTERFEROMETER

In its investigation of mine gases the Bureau of Mines has tested the laboratory-type Rayleigh interferometer as adapted to gas analysis by Haber of Berlin and Löwe of Jena, and made by Zeiss of Jena. Mohr,³⁷ Haber,³⁸ Löwe,³⁹ and Küppers⁴⁰ have published studies concerning its use.

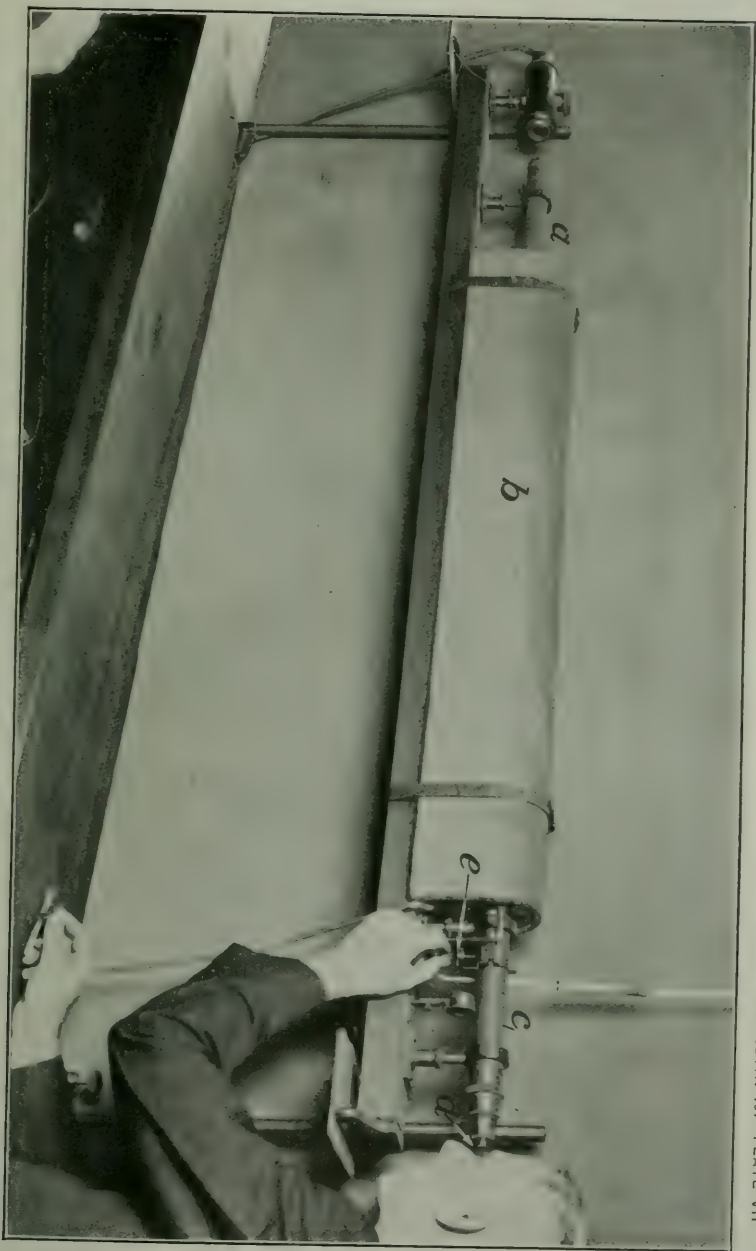
The instrument is made in two different models. The laboratory type (Pl. VII and fig. 25) is of rigid construction, has gas chambers 1 meter long, and is employed for exact gas analysis. It corresponds to apparatus that use mercury as the confining fluid, and with which results accurate to 0.02 to 0.03 per cent can be obtained. Some experience is required before one becomes sure of the readings. The laboratory type only is discussed here.

³⁷ Mohr, O., Die Verwändung des zeisschen Interferometers zur technischen Rauchgasanalyse: Ztschr. angew. Chem., Jahrg. 25, June 28, 1912, pp. 1313, 1317.

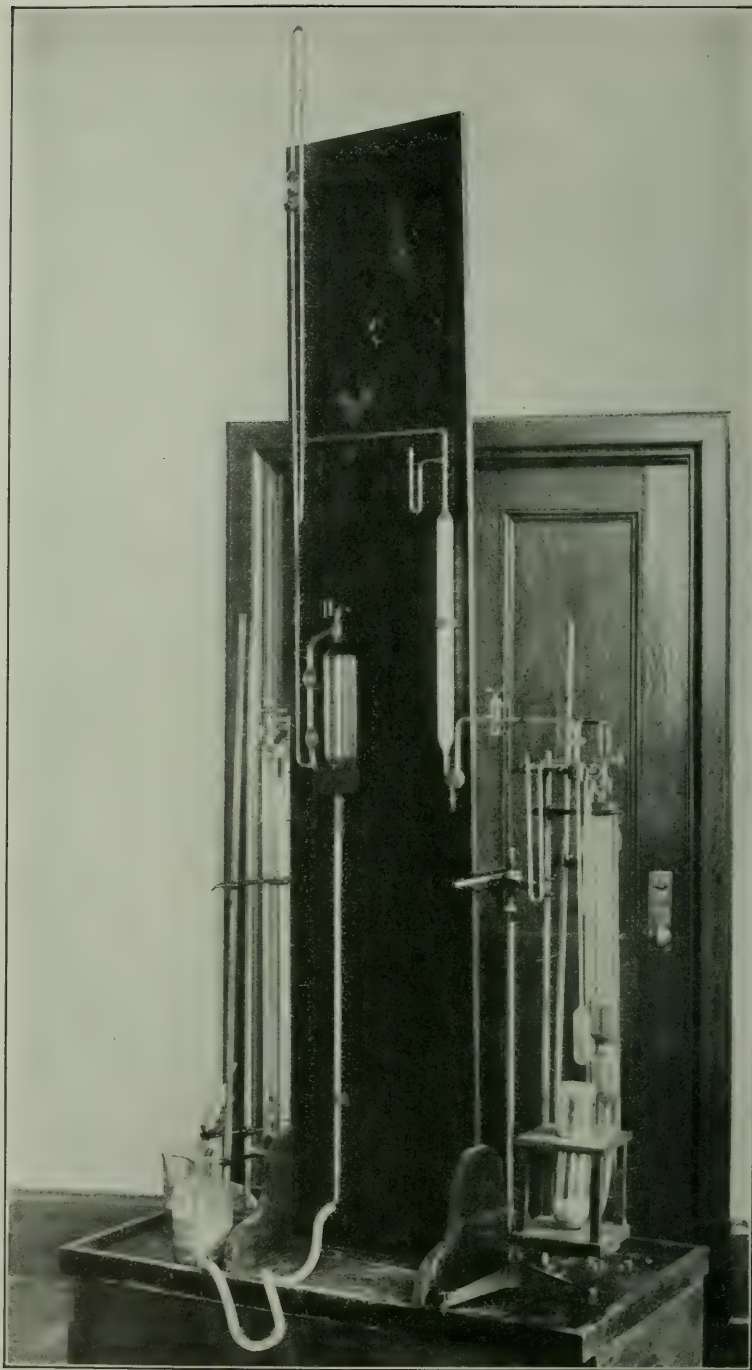
³⁸ Haber, F., Optische Analyse der Industriegase: Ztschr. angew. Chem., Jahrg. 19, Aug. 17, 1906, p. 1418-1422.

³⁹ Löwe, F., Ein neues Interferometer für Gase und Flüssigkeiten: Physikal. Ztschr., Jahrg. 11, No. 23, 1910, pp. 1047-1051.

⁴⁰ Küppers, E., Die Bestimmung des Methangehaltes der Wetterproben mit Hilfe des tragbaren Interferometers: Glückauf, Jahrg. 49, Jan. 11, 1913, pp. 47-50.



LABORATORY TYPE OF INTERFEROMETER



APPARATUS FOR FRACTIONATION OF NATURAL GAS AT LOW TEMPERATURES AND PRESSURES

The other model, the short or portable type, is employed for the analysis of gas mixtures when extreme accuracy is not required. Its accuracy is about 0.2 to 0.3 per cent and is comparable with that usually obtained in technical gas analysis when water is employed as the confining fluid. Both instruments depend upon the same principle. The short model is constructed with a view to portability. When in position it is upright, about 10 cm. in diameter and 50 cm. high, and weighs about 11 pounds.

DESCRIPTION OF LABORATORY TYPE

Figure 25 illustrates the principle of operation of the laboratory type. The pencil of parallel rays which comes from the light of a Nernst lamp passes through the object glass of the collimator *c* and travels in three parts to the observation telescope *d*. The upper

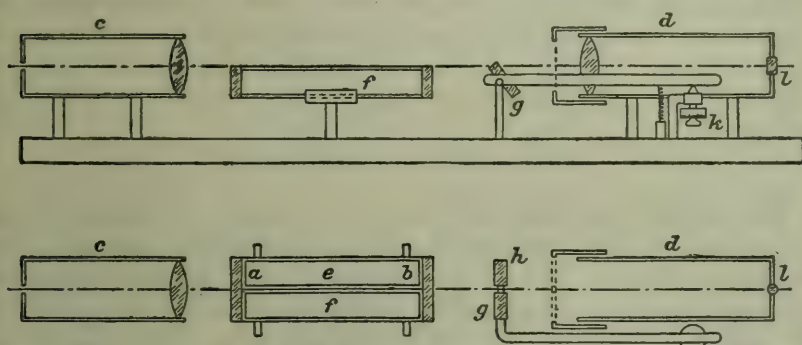


FIGURE 25.—Diagram of parts of laboratory interferometer, vertical and horizontal sections. For explanation, see text

half of the pencil, in shape of a half cylinder, passes directly toward a double diaphragm placed at the end of the object glass of the telescope and covering all of the object glass. This pencil of rays passes through the diaphragm into the upper half of the object glass of the telescope. In its focal plane this part of the pencil of rays produces an image of the slit, together with Fraunhofer's diffraction phenomena, which consist of two straight parallel dark bands in a white field, with colored bands on each side. The lower half of the pencil of rays is divided into two parts by the metallic partition *ab*. One part passes through the gas chamber *e* and the other through chamber *f*, which contains the gas for comparison. The pencil of rays also passes through compensator plates *h* and *g*. The part *h* is movable by means of a micrometer screw, *k*, which measures the deflection of the plate. The part *g* is fixed. By this arrangement the optical path of the gas in chamber *e* can be varied. From the compensator plates the rays pass through the diaphragm into the telescope.

The phenomena produced by the pencil of rays passing through the system are viewed by a strongly magnifying cylindrical eyepiece, *l*, because the dark interferometer bands, being only a few hundredths of a millimeter apart, could not otherwise be distinguished. The band image of the upper half of the rays remains constant during all the operations. If the two chambers *e* and *f* are filled with the same gas at the same temperature and pressure, and the compensator plates are perfectly parallel, the interference phenomena produced can not be distinguished from those produced by the upper half of the rays. If, however, pure dry air freed from carbon dioxide is introduced into chamber *f*, and pure dry air containing carbon dioxide is placed in chamber *e*, the lower band image is shifted laterally. Manipulation of screw *k* brings the bands back to their original position, the zero position on the screw. The difference of the readings on the graduated screw before and after the gas mixture is introduced is a measure of the refractive difference of the two gases. It must be remembered that the gases in the two chambers must have the same temperature and pressure and must be dry.

CALIBRATION OF INSTRUMENT

The authors have calibrated the interferometer by comparing the indications of this instrument with determinations by an exact analytical method. When one constituent of a gas mixture is determined the absolute refraction coefficients should differ by 0.0001 to possess an accuracy of about 0.02 per cent. The greater the difference of absolute refraction coefficients the greater is the accuracy of the method. Consequently, if carbon monoxide, nitrogen, or oxygen dilutes the air, the interferometer does not give accurate results, because the absolute refraction coefficients of those gases differ only in the fifth decimal place. If air always had to be used as a gas of comparison a serious limitation would be placed upon the interferometer. Fortunately this is not so. Pure air is used only when a constituent that contaminates pure air is to be determined. The general rule can be stated that the standard gas, or that used in the chamber as the gas of comparison, is the same as that in the chamber containing the gas to be tested, except that the constituent to be determined is removed from the standard gas by some suitable means. The difference in refraction is then due solely to the constituent the determination of which is sought.

RESULTS FROM USE OF THE INSTRUMENT

The authors have utilized the interferometer in analyzing mixtures of air and carbon dioxide, air and methane, and air and Pitts-

burgh natural gas; and they have also determined the effect of lowering the oxygen content in mixtures of air and carbon dioxide and of air and methane.

Results of the analysis of mixtures of CO_2 and air by means of the interferometer and by gas analysis (Pl. III) are shown below. With the eudiometer the results are accurate to within 0.02 per cent.

Results of analyses of mixtures of carbon dioxide and air

CO ₂ as determined by interferometer *	CO ₂ as determined by eudiometer		CO ₂ represented by one drum division
	First analysis	Duplicate analysis	
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.09	0.10	0.12	0.01222
1.12	.11	.13	.01000
.28	.26	.28	.00964
.77	.76	.79	.0100
.79	.80	.84	.0104
.64	1.63	1.60	.00984
2.56	2.52	2.55	.00990
3.65	3.67	3.68	.01007
4.77	4.72	4.73	.00990
8.76	8.78	8.81	.01004

* Difference between zero and final readings in drum divisions on the micrometer screw.

The results of analyses of mixtures of methane and air follow. Such proportions of methane as frequently occur in mine air were used. All eudiometric analyses were made by means of the modified Haldane gas-analysis apparatus shown.

In making tests with the interferometer, the standard gas was passed into the comparison chamber at atmospheric temperature and pressure. The gas to be tested was then passed into the test chamber. When readings were taken the flow of gas to be tested was interrupted, and its pressure brought to atmospheric by opening one of the rubber connecting tubes to the air. When readings were promptly taken, diffusion of outside air back into the gas chambers was not appreciable. Soda lime, calcium chloride, and sulphuric acid were used where needed to purify the gases.

Results of analyses of mixtures of methane and air

CH ₄ as determined by interferometer *	CH ₄ as determined by eudiometer		CH ₄ represented by one drum division
	First analysis	Duplicate analysis	
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.03	0.04	-----	0.01333
.12	.12	0.12	.01000
.42	.41	.41	.00976
.84	.86	.89	.01042
1.54	1.53	1.55	.01000

* Difference between zero and final readings in drum divisions on the micrometer screw.

EFFECT OF LOWERING OXYGEN CONTENT OF MIXTURES ANALYZED

As oxygen and nitrogen are not present in some mixtures in the proportions found in atmospheric air, some experiments were made to ascertain the effect due to less oxygen and more nitrogen than are present in air. The results are tabulated below. Of the two tabulations, the first shows the effect of decreasing the oxygen content of mixtures of CO_2 and air and the second the effect of decreasing the oxygen content of mixtures of methane and air.

Effect of lowering the oxygen content of mixtures of carbon dioxide and air

1	2	3	4	5
CO_2 indicated by interferometer	CO_2 indicated by analysis	Oxygen indicated by analysis	Difference in oxygen content as compared with that of normal air	$\frac{\text{Column 1}-\text{column 2}}{\text{Column 4}}$
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.20	0.20	20.77	0.16	0.135
.50	.40	20.19	.74	.103
.71	.63	20.15	.78	.155
.57	.43	20.03	.90	.128
.89	.76	19.92	1.01	.160
1.36	1.10	19.31	1.62	.162
.53	.25	19.20	1.73	

Therefore, for every 1 per cent decrease in oxygen and a corresponding increase in nitrogen, the CO_2 determined by the interferometer will appear about 0.15 per cent too high if normal air is used as the gas of comparison.

Effect of lowering the oxygen content of mixtures of methane and air

Methane indicated by interferometer	Methane indicated by analysis	Oxygen indicated by analysis	Difference in oxygen content as compared with that of normal air	$\frac{\text{Column 1}-\text{column 2}}{\text{Column 4}}$
1	2	3	4	5
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.11	0.08	20.53	0.40	0.174
.18	.17	20.36	.57	.179
.84	.66	19.90	1.03	.138
.44	.16	19.36	1.57	.150
.42	.20	19.33	1.60	.167
.48	.21	19.13	1.80	.179
1.58	1.18	18.53	2.40	
.95	.46	18.20	2.73	

On the basis of the results presented above the following statements may be made: For every 1 per cent decrease in oxygen and a

corresponding increase in nitrogen the proportion of CO_2 determined by the interferometer will appear about 0.15 too high if normal air is used as the gas of comparison, and for every 1 per cent decrease in oxygen and a corresponding increase of nitrogen the proportion of methane as indicated by the interferometer will appear about 0.16 per cent too high if normal air is used as the gas of comparison.

For application of the interferometer to other gases not mentioned is given a table of values of absolute indexes of refraction of the commonly occurring gases:⁴¹

Values of absolute indexes of refraction (0° C. and 760 mm. Hg pressure)

Gas	Value	Gas	Value
Hydrogen.....	1.000139	Nitrous oxide.....	1.000505
Water vapor.....	1.000261	Acetylene.....	1.000610
Oxygen.....	1.000270	Hydrogen sulphide.....	1.000644
Nitrogen.....	1.000297	Sulphurous acid.....	1.000665
Air.....	1.000293	Ethylene.....	1.000678
Nitric oxide.....	1.000300	Chlorine.....	1.000772
Carbon monoxide.....	1.000340	Cyanide.....	1.000834
Ammonia.....	1.000381	Benzol vapor.....	1.001700
Methane.....	1.000444	Pentane vapor.....	1.001711
Hydrogen chloride.....	1.000449		

CONCLUSIONS REGARDING THE INTERFEROMETER

The interferometer can be successfully used for technical gas analysis, especially for these tests and determinations: Tests of mine air for CO_2 and CH_4 ; tests of the purity of manufactured hydrogen, chlorine, and other gases; determination of CO_2 in flue gases and breathing air; determination of sulphur dioxide in gases in connection with sulphuric acid manufacture; and others. Haber⁴² has used the interferometer in determining the ammonia content of gases in the production of synthetic ammonia.

Mohr⁴³ has used the interferometer for analyzing flue gases. In Mohr's method the gas, after going through a drying tube, was passed through the interferometer and through a tube containing soda lime to absorb the CO_2 , then the gas was again passed into the interferometer. After the absorption of the CO_2 the reading, of course, gave a different value than that obtained before absorption.

The difference between the two values when referred to prior calibration for CO_2 gave the percentage content of CO_2 . The flue gas freed from CO_2 (no account being taken of the small quantities of

⁴¹ Seibert, F. M., and Harpster, W. C., Use of the interferometer in gas analysis: Tech. Paper 185, Bureau of Mines, 1918, 18 pp.

⁴² Haber, F., and Le Rossignol, R., The production of synthetic ammonia: Jour. Ind. Eng. Chem., vol. 5, 1913, pp. 328-330.

⁴³ Mohr, O., Die Verwendung des zeisschen Interferometers zur technische Rauchgasanalyse: Ztsch. angew. Chem., Jahrg. 25, June 24, 1912, pp. 1313-1317.

H_2 , CH_4 , and CO) does not have the same refractive exponent; consequently, Mohr calibrated the instrument with varying proportions of carbon dioxide, nitrogen, and oxygen. The oxygen content was estimated from a table prepared from the indications of the interferometer but as the sum ($CO_2 + O_2$) is not 20.9 per cent, and varies considerably with the fuel used, the results become only approximate, as to insure accuracy too many varying factors must be known.

The instrument can be used to determine methane in mine air if a suitable gas of comparison is employed; in other words, for comparison, the same mine air must be used as that whose methane content is to be determined, except that the methane in the gas (air) used for comparison must be removed by burning it and absorbing the carbon dioxide produced. However, if the mine air does not differ appreciably from atmospheric air, the latter can be used in the comparison chamber, but if the oxygen content of the mine air is much lower than that of atmospheric air, the proportion of methane will appear too great, as will be seen from the results in the table headed "Effect of lowering oxygen content of mixture of methane and air." As the oxygen content of mine air is seldom much lower than that of atmospheric air, the interferometer becomes generally applicable to the determination of CH_4 and CO_2 in mine air.

Küppers⁴⁴ has used the portable interferometer to determine methane in normal mine air, and his results agree rather closely with those obtained by ordinary analytical methods.

APPARATUS FOR ANALYZING NATURAL GAS

With a view to gathering data on the composition and fuel value of natural gas, the Bureau of Mines has been collecting samples of gas from different gas and petroleum fields. The natural gas piped to Pittsburgh is used at the Pittsburgh experiment station in making tests of explosives, flame safety lamps, electric mine motors, and so on, consequently the bureau has studied the composition of this gas to determine its explosive limits.⁴⁵ Analyses of natural gas from the southern California oil fields have also been reported.⁴⁶ Additional samples have been collected in West Virginia, Alabama, Nevada, Louisiana, Utah, Washington, Oklahoma, Kansas, Pennsylvania, Tennessee, Ohio, Kentucky, and Oregon.

⁴⁴ Küppers, A., Die Bestimmung des Methangehaltes der Wetterproben mit Hilfe des tragbaren Interferometers: Glückauf, Jahrg. 49, Jan. 11, 1913, pp. 47-50.

⁴⁵ Hall, Clarence, Snelling, W. O., and Howell, S. P., Investigations of explosives used in coal mines, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by Charles E. Munroe: Bull. 15, Bureau of Mines, 1912, pp. 63-77.

⁴⁶ Allen, I. C., and Jacobs, W. A., Physical and chemical properties of the petroleum of the San Joaquin Valley, Calif., with a chapter on analyses of natural gas from the southern California oil fields, by G. A. Burrell: Bull. 19, Bureau of Mines, 1911, p. 56.

Samples of natural gas supplied to larger cities in the United States have been collected and analyzed,⁴⁷ and tests have been conducted with reference to the compressibility of natural gas,⁴⁸ the conditions under which it exists underground,⁴⁹ and the variation in composition of natural gas from different sands in the same fields.⁵⁰

CONSTITUENTS OF NATURAL GAS

Accurate determination of the constituents of natural gas has proved a stumbling block to gas analysts unfamiliar with the work. Technical forms of gas-analysis apparatus and established rules for bringing a gas mixture in contact with the absorbents for different constituents are not always effective. Many samples contain absorbable constituents, such as carbon dioxide and oxygen, in extremely small quantities. The fact that oxygen may be a constant constituent of natural gas as it leaves a well has not been determined absolutely. The authors believe that the traces of oxygen reported in some samples were due to contamination of the samples with air. Phillips⁵¹ detected only minute quantities of oxygen in natural gas from western Pennsylvania after the gas had bubbled continuously for many hours or days through reagents.

Olefin hydrocarbons and carbon monoxide have not been identified in the samples already received at the bureau's Pittsburgh laboratory, if the natural gas had not been mixed with artificial gas. Because higher members of the paraffin series are absorbed by fuming sulphuric acid and cuprous chloride, a natural gas that does not contain olefin hydrocarbons or carbon monoxide but does contain these higher members of the paraffin series, when treated with these solutions will undergo a reduction in volume and lead the analyst to a wrong conclusion.

Natural gas usually contains a large proportion of paraffin hydrocarbons, some samples as much as 99 per cent, so that if the paraffins are determined by explosion methods in which a small quantity (8 or 10 c. c.) of gas is used a slight error of manipulation will be

⁴⁷ Burrell, G. A., and Oberfell, G. G., Composition of natural gas used in 25 cities, with a discussion of the properties of natural gas: Tech. Paper 109, Bureau of Mines, 1915, 22 pp.

⁴⁸ Burrell, G. A., and Robertson, I. W., Compressibility of natural gas at high pressures: Tech. Paper 131, Bureau of Mines, 1916, 11 pp. Burrell, G. A., and Robertson, I. W., Compressibility of the constituents of natural gas, with composition of the natural gas used in 31 cities in the United States: Tech. Paper 158, Bureau of Mines, 1917, 16 pp.

⁴⁹ Burrell, G. A., Condition of natural gas in the earth's strata: Jour. Ind. Eng. Chem., vol. 7, 1915, p. 322.

⁵⁰ Burrell, G. A., and Oberfell, G. G., Variation in composition of natural gas from different sands in the same field: Jour. Ind. Eng. Chem., vol. 7, 1915, p. 419. Burrell, G. A., and Seibert, F. M., Separation of the constituents in natural gas from which natural gas is condensed: Jour. Am. Chem. Soc., vol. 37, 1915, p. 392.

⁵¹ Phillips, F. C., Composition of natural gas; researches upon the phenomena and chemical properties of gases: Am. Chem. Jour., vol. 16, 1894, p. 411.

multiplied 10 or 12 times in calculating results to a percentage basis. Methane is the only hydrocarbon that some natural gases contain; but if a small quantity of sample is taken for the combustion analysis, errors are magnified. The relation between the volume of carbon dioxide and the contraction produced by the combustion may indicate hydrogen, although this gas is absent. Although the error in the observed data may be small, by calculation to a percentage basis it may amount to several per cent of hydrogen. Many published analyses of natural gas are undoubtedly much in error from such causes.

The paraffin hydrocarbons that are gaseous at ordinary temperatures are methane, ethane, propane, and butane. Since the last two are liquefied at ordinary temperatures by pressures below those existing in most producing wells, quantities other than small proportions carried by the permanent gases would hardly be found in natural gases coming from wells under very high pressure. On the other hand, gases drawn from wells under a partial vacuum may contain large amounts of these and higher paraffins.

METHOD OF SAMPLING

Some samples of gas taken by the bureau's investigators are collected in magnesium citrate bottles by air displacement. At the wells or supply pipes a stopper is removed and gas allowed to run into the bottle until air has been entirely displaced. Five or more minutes are usually enough. The stopper is inserted while the bottle is still in place. As a precaution against leakage, melted paraffin is poured over the stopper. The bottles are then carefully packed in suitable wooden boxes and sent to the bureau's Pittsburgh laboratory. There the stoppers are removed under mercury, and the gas is transferred to and analyzed in an apparatus that contains mercury as the confining fluid. Some samples taken at the full pressure of the well have been received in strong iron cylinders. Other samples have been collected by a method devised by G. A. Hulett, former chief chemist of the Bureau of Mines, which is now used for collecting some of the bureau's samples of natural gas. It is as follows:

Use a glass tube about 17 cm. long and 6 cm. wide which has a 15-cm. glass-tube extension at one end with a 6-mm. bore. Leave the tube open. Direct natural gas into the sampling tube through the orifice by means of a long slender brass tube. When the air originally in the tube has been displaced, withdraw the brass tube and close the glass-tube orifice by placing the finger over it. Carry the sampling tube to a small alcohol flame and seal the extension.

SIMPLIFIED APPARATUS USED IN ANALYZING NATURAL GAS

Figure 26 shows the apparatus used to analyze natural gas. Pipette *a* contains potassium hydroxide solution; pipettes *b* and *d* contain alkaline pyrogallate solution. Pipette *c* is the slow-combustion pipette. The burette has a capacity of 100 c. c. and is graduated to 0.1 c. c.

PROCEDURE OF ANALYSIS

Natural gas is analyzed at the bureau's Pittsburgh laboratory as follows:

Displace oxygen or other gas left in the horizontal capillary train by drawing a few cubic centimeters of nitrogen from pipette *d* into the burette; then allow this mixture to escape into the atmosphere.

Draw, by mercury displacement, about 100 c. c. of the gas sample from the sample container into the burette. Measure the sample in the burette against the pressure in compensating tube *f* by bringing the mercury in the manometer tube exactly to mark *g*. Pass the sample first into the potassium hydroxide and then into the alkaline pyrogallate solution to remove carbon dioxide and oxygen, making burette measurements in the same manner as with the original sample.

COMBUSTION ANALYSIS

Discard the residual gas left after the carbon dioxide and oxygen have been determined, and take a fresh part of the sample for the combustion analysis. Clear the capillary connections of combustible gas by dilution with air, and measure about 100 c. c. of oxygen into the burette and pass it into the combustion pipette. Draw about 35 c. c. of the gas sample into the burette from the sample container and measure it. Heat the platinum wire in the combustion pipette to a white heat, and pass the gas sample at the rate of about 10 c. c. per minute into the combustion pipette containing the oxygen. The paraffins burn as fast as they enter, so that an explosion caused by an accumulation of gas and oxygen can not follow. In analyzing natural gas the authors have

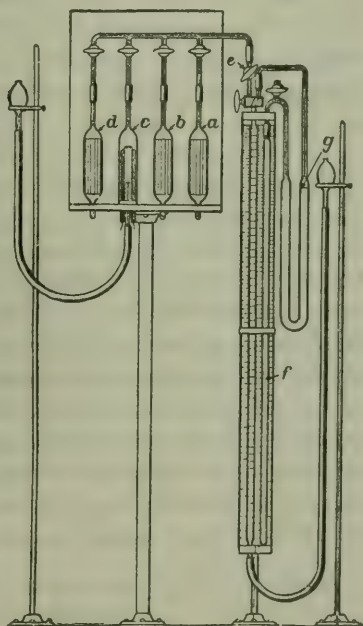


FIGURE 26.—Laboratory apparatus for analysis of natural gas. For explanation, see text

obtained the best results by passing the oxygen into the pipette first. When the natural gas is passed in first, the mixture does not always burn as satisfactorily.

After the paraffins have burned, which requires about 4 or 5 minutes, cool the combustion pipette and measure the contraction in volume due to combustion. Determine the carbon dioxide produced by the combustion by absorption in the potassium hydroxide solution. Finally, pass the gas into the alkaline pyrogallate solution to make sure that enough oxygen has been present for complete oxidation of the paraffins. Some samples may contain such a large proportion of the higher-paraffin hydrocarbons that 100 c. c. of oxygen will not be enough for complete oxidation of 35 c. c. of natural gas. For such samples use a smaller quantity of the gas for the combustion. This statement has special reference to those natural gases that are used for gasoline manufacture and contain a large percentage of the higher paraffins.

PRECAUTIONS

Never raise the burette mercury above the upper stopcock. Bring the gas remaining in the capillary tubing at any stage of the analysis in contact with the solution by passing it back and forth several times between the burette and the pipette. For instance, after combustion, some carbon dioxide will remain in the capillary tubing between the combustion pipette and the burette when the gas is drawn back into the burette to record the contraction in volume. After most of the carbon dioxide has been absorbed by the passage of the gas into the potassium hydroxide pipette, sweep out the small quantity of carbon dioxide in the capillary tubing into the potassium hydroxide pipette. Repeat to insure complete removal of the carbon dioxide. If this precaution is not taken, a serious error will result.

QUALITATIVE TESTS FOR CARBON MONOXIDE AND OLEFIN HYDROCARBONS IN NATURAL GAS

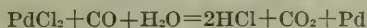
The blood test for carbon monoxide and the iodine pentoxide and palladium chloride tests for carbon monoxide and olefin hydrocarbons are used at the bureau's Pittsburgh laboratory in analyzing natural gases.

A dilute solution of palladium chloride undergoes reduction in the presence of olefin hydrocarbons or carbon monoxide.⁵² The reaction is marked even when traces of these constituents are present in a gas mixture. Palladium separates out as a black cast, or as particles suspended throughout the liquid. The authors found that 0.1 per cent of ethylene in a mixture of ethylene and air could

⁵² Phillips, F. C., *Researches upon the oxidation and chemical properties of gases*: *Am. Chem. Jour.*, vol. 16, 1894, p. 267.

be detected by the appearance of precipitated palladium when 200 c. c. of the mixture was passed through a 0.5 per cent solution of palladium chloride at the rate of 10 c. c. per minute. The reaction becomes more marked when the gas is shaken in a test tube for about 10 minutes with the palladium chloride solution.

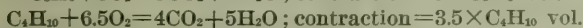
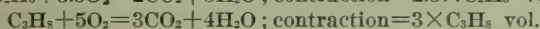
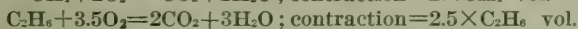
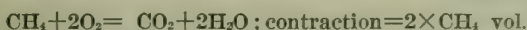
Carbon monoxide in a gas mixture in the same proportion and under the same conditions produces a precipitation of palladium from palladium chloride. Carbon monoxide combines with palladium chloride according to the following reaction:



The reaction of palladium chloride on ethylene does not produce carbon dioxide.

CALCULATIONS FROM COMBUSTION DATA

If the contraction and the volume of carbon dioxide from the combustion of the gas indicate methane only, this constituent is reported; but if the data indicate higher members of the paraffin series, a calculation is made that gives the two predominating constituents. The gaseous hydrocarbons react with oxygen as follows:



But since the experiments of Rayleigh, Leduc, Baumè, Perrot, and others have shown that some gases deviate somewhat from the gas laws,⁵³ corrections must be made for some gas analyses where this deviation is greater than the experimental error.

Below is a table of the theoretical and observed specific gravities of the gases involved in the calculations; it is taken from Landolt and Börnstein.⁵⁴

Theoretical and observed specific gravities of certain gases at 0° C. and 760 mm. pressure

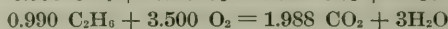
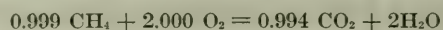
Gas	Molecular weight	Specific gravity		Observer	Theoretical, observed
		Theoretical	Observed		
CH ₄	16.03	0.5539	0.5544	Baumè and Perrot.....	0.999
C ₂ H ₆	30.05	1.0381	1.0494	do.....	.990
C ₄ H ₁₀	58.05	2.0065	2.01	Frankland.....	.998
CO.....	28.00	.9673	.96702	Leduc.....	1.000
CO.....	28.00	.9673	.96716	Rayleigh.....	1.000
CO ₂	44.00	1.5201	1.52874	Leduc.....	.994
CO ₂	44.00	1.5201	1.52909	Rayleigh.....	.994
N ₂	28.08	.9680	.96737	do.....	1.001
N ₂	28.08	.9680	.96717	Leduc.....	1.001
O ₂	32.00	1.1055	1.10535	Rayleigh.....	1.000
O ₂	32.00	1.1055	1.10523	Leduc.....	1.000

⁵³ Burrell, G. A., and Seibert, F. M., Errors in gas analysis due to the assumption that the molecular volumes of all gases are alike: Tech. Paper 54, Bureau of Mines, 1913, 16 pp.

⁵⁴ Landolt, H., and Börnstein, R., *Physikalisch-chemische Tabellen*. 3d ed., 1905, pp. 222-223; Jour. Chem. Phys., vol. 7, 1909, p. 367.

REACTIONS OF METHANE AND ETHANE WITH OXYGEN

Below are the equations for the reactions of methane and ethane with oxygen, in which corrections have been made according to the specific gravity determinations shown in the preceding table:



MOLECULAR VOLUME OF CARBON DIOXIDE AT DIFFERENT PARTIAL PRESSURES

As the partial pressure of gases in a mixture decreases the gases more nearly conform in behavior to the gas laws; consequently, a table is included herein which shows the correct molecular volume to use for carbon dioxide at different partial pressures. The partial pressure of the carbon dioxide refers to the ratio of the volume occupied by the carbon dioxide found after the combustion to the total volume of residual gas found after the combustion; that is, if the total volume after combustion is found to be 70 c. c. and the carbon dioxide is 40 c. c. the partial pressure of the carbon dioxide will be $\frac{40 \times 760}{70} = 434$ mm., and the proper molecular volume—0.997—will be found from the table.

The foregoing equations refer to gases at 0° C. and 760 mm. pressure. The following table shows the correct molecular volumes for carbon dioxide at 20° C. and different partial pressures:

Molecular volume of carbon dioxide corresponding to different partial pressures at 20° C.

Mercury, mm.	Molecular volume	Mercury, mm.	Molecular volume
100.....	0.9993	500.....	0.9965
200.....	.9986	600.....	.9958
300.....	.9980	700.....	.9951
400.....	.9972	760.....	.9950

In compiling this table advantage was taken of the work of Rayleigh,⁵⁵ Leduc, and Chappius on the determination of the specific gravity and coefficient of expansion of carbon dioxide. The specific gravity determinations were given by Rayleigh and Leduc for carbon dioxide at 0° C. and 760 mm. pressure. Values for 20° C. and 760 mm. pressure were determined from the coefficient of expansion of carbon dioxide between 0° C. and 20° C. A graph was plotted from two values, the deviation from the gas laws at 760 mm. pressure and at 380 mm. pressure.

The coefficient of expansion of ethane between 0° and 20° C. has not been determined, consequently the same molecular volume was used at 20° C., the laboratory working temperature, as was reported by Baumé

⁵⁵ Landolt, H., and Börnstein, R., *Physikalisch-chemische Tabellen*. 1912, p. 148.

and Perrot⁵⁶ at 0° C. The error resulting from this usage can be disregarded without introducing any appreciable error in the analyses, judging from the molecular volume of carbon dioxide, which at 20° C. differs only 0.001 from the value at 0° C.

Below are the molecular volumes to be used for ethane at different partial pressures:

Molecular volume of ethane corresponding to different partial pressures

Mercury, mm.	Molecular volume	Mercury, mm.	Molecular volume
0.....	1.000	500.....	0.993
100.....	.999	600.....	.992
200.....	.997	700.....	.991
300.....	.996	760.....	.990
400.....	.995		

Although the individual paraffins in a mixture of several can not be determined exactly, the chemist will know accurately enough which value in the above column to use by accepting the value that corresponds to the percentage of ethane determined from the combustion analysis. Moreover, the partial pressure of ethane in natural gas from many places is so low that there is only slight deviation from the gas laws. A slight error arises from the probable percentage of propane or butane in a mixture when the combustion analysis indicates methane and ethane only, but the partial pressures of the propane and butane will usually be so low that errors in molecular volume due to their presence can be disregarded.

Methane conforms so closely to the gas laws that no deviation from the given molecular volume need be made for different partial pressures.

The proper equations to use can be determined only from the partial pressures obtained from the analyses. To determine the approximate percentage of ethane the theoretical equations can be used.

APPLICATION OF THE USE OF CORRECTED EQUATIONS TO THE ANALYSES OF NATURAL GAS AND OTHER GAS MIXTURES

Although the combustion analysis does not show an accurate distribution of hydrocarbons in a natural-gas mixture, it does show the true total paraffin content. The heating value calculated from such an analysis is also correct.

Determinations by the slow-combustion method show that the natural gas supplied to Pittsburgh from Appalachian fields contains about 83 per cent CH_4 , 16 per cent C_2H_6 , and 1 per cent N_2 . These proportions vary from time to time during the year. This gas is almost all methane, but contains small amounts of ethane and pro-

⁵⁶ Landolt, H., and Börnstein, R. Work cited, p. 148.

pane and some of the higher homologues. A typical analysis with the calculation from the analytical data is given herewith.

Typical analysis and calculation of natural gas

Stages in analysis:	Burette readings, c. c.
Sample taken.....	30.70
Volume after CO ₂ absorption.....	30.70
Portion taken for combustion.....	30.70
Oxygen added.....	74.85
Total volume.....	105.55
Volume after burning.....	42.30
Contraction.....	63.25
Volume after CO ₂ absorption.....	7.20
Carbon dioxide.....	35.10

CH₄ and C₂H₆ are calculated from the theoretical equations as follows:

$$\begin{aligned}
 &\text{Let } x = \text{methane.} \\
 &\text{and } y = \text{ethane.} \\
 &\text{Then } 2x + 2.5y = \text{total contraction.} \\
 &\text{and } x + 2.0y = \text{CO}_2 \text{ produced.} \\
 &\text{C}_2\text{H}_6 = 15.1 \text{ per cent.} \\
 &\text{CH}_4 = 84.1 \text{ per cent.} \\
 &\text{Total paraffins} = 99.2 \text{ per cent.}
 \end{aligned}$$

They are calculated from the corrected equation as follows:

$$\begin{aligned}
 &\text{Let } x = \text{methane.} \\
 &\text{and } y = \text{ethane.} \\
 &\text{Then } 2.004x + 2.5y = \text{total contraction,} \\
 &\text{and } 0.996x + 2.0y = \text{CO}_2 \text{ produced.} \\
 &\text{C}_2\text{H}_6 = 15.7 \text{ per cent.} \\
 &\text{CH}_4 = 83.1 \text{ per cent.} \\
 &\text{Total paraffins} = 98.8 \text{ per cent.}
 \end{aligned}$$

ANALYSIS OF GAS CONTAINING HIGH PERCENTAGES OF CO

An interesting situation develops when a mixture containing a high percentage of carbon monoxide is analyzed. Carbon monoxide was prepared from oxalic acid and sulphuric acid in the usual way, and the gas after purifying was analyzed by the slow-combustion method.

Observed data in an analysis of a mixture containing a high percentage of carbon monoxide

Stages in analysis:	Burette readings, c. c.
Sample taken.....	51.00
Volume after carbon dioxide absorption.....	51.00
Portion taken for combustion.....	51.00
Oxygen added.....	32.80
Total volume.....	83.80
Volume after burning.....	58.70
Contraction.....	25.10
Volume after carbon dioxide absorption.....	9.30
Carbon dioxide.....	49.40
Corrected percentage of CO, 97.3.	

Some air was present in the mixture. According to the equation, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, the CO is double the contraction, and the CO is equivalent to the CO_2 . The CO_2 produced by the combustion should be just twice the contraction, but it will be noticed that a difference of 0.8 c. c. exists between the observed result and the theoretical; that is,

$$2 \times 25.1 = 50.2 \text{ c. c.}$$

$$\text{and } 50.2 \text{ c. c.} - 49.4 \text{ c. c.} = 0.8 \text{ c. c.}$$

$$2.000 \text{ CO} + 1.000 \text{ O}_2 = 1.992 \text{ CO}_2.$$

When the correct molecular volumes are used the equation becomes

$$1.984 \text{ (contraction)} = \text{CO}$$

$$1.004 \text{ (CO}_2\text{)} = \text{CO}$$

$$1.984 \times 25.1 \text{ c. c.} = 49.80 \text{ c. c. CO}$$

$$1.004 \times 49.4 \text{ c. c.} = 49.60 \text{ c. c. CO}$$

or $49.80 \text{ c. c.} - 49.6 \text{ c. c.} = 0.20 \text{ c. c.}$, which is only slightly greater than the experimental error of the apparatus.

ANALYSIS OF METHANE

For methane the correction is small. CH_4 prepared by the method of Gladstone and Tribe⁵⁷ and containing a small quantity of air analyzed as follows:

Observed data in analysis of methane

Stages in analysis:	Burette readings, c. c.
Sample taken-----	30.40
Volume after carbon dioxide absorption-----	30.40
Portion taken for combustion-----	30.40
Oxygen added-----	66.65
Total volume-----	97.05
Volume after burning-----	37.15
Contraction-----	59.90
Volume after carbon dioxide absorption-----	7.35
Carbon dioxide-----	29.80

Corrected percentage of CH_4 , 98.4.

Methane reacts with oxygen according to the theoretical equation, as follows:

$$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$$

$$\frac{\text{contraction}}{2} = \text{CH}_4 = \text{CO}_2$$

According to these equations the percentage of CH_4 becomes 98.0 per cent. When calculated from the correction basis the equation becomes:

$$1.000 \text{ CH}_4 + 2.000 \text{ O}_2 = 0.996 \text{ CO}_2 + 2\text{H}_2\text{O}$$

$$\text{then } 0.499 \text{ (contraction)} = \text{CH}_4$$

$$\text{and } 1.004 \text{ (CO}_2\text{)} = \text{CH}_4$$

which gives 98.4 CH_4 when calculated from the CO_2 .

⁵⁷ Gladstone, T. H., and Tribe, Alfred. Note on the preparation of marsh gas: Jour. Chem. Soc., vol. 45, 1884, p. 154.

The difference in the percentages when calculated from the corrected and the theoretical equations is $98.4 - 98.0 = 0.4$ per cent.

When the results are calculated from the contraction there is a difference between the theoretical and corrected values of $98.5 - 98.3 = 0.2$ per cent.

ANALYSIS OF ETHANE

Ethane prepared by the method of Gladstone and Tribe⁵⁸ and mixed with air gave the following analysis:

Observed data in analysis of ethane

Stages in analysis:	Burette readings, c. c.
Sample taken.....	20.20
Volume after carbon dioxide absorption.....	20.20
Portion taken for combustion.....	20.20
Oxygen added.....	80.50
Total volume.....	100.50
Volume after burning.....	50.20
Contraction.....	50.30
Volume after carbon dioxide absorption.....	10.20
Carbon dioxide.....	40.00

From the theoretical equation $C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$, the C_2H_6 in the mixture becomes 100 per cent. According to the corrected equation, $C_2H_6 = 99.4$ per cent, or a difference of 0.6 per cent, when calculated from the CO_2 produced. When the calculations are made from the contraction there is a difference between the theoretical and the corrected values of $100.6 - 99.6 = 1.0$ per cent.

CORRECTION FOR OTHER GASES

Because gases conform more nearly to the gas laws as their partial pressures become further removed from 760 mm. of mercury, certain gases that are noteworthy because they do not conform to these laws may be in a mixture and do not need to have their volumes corrected if their partial pressures are reduced much below 1 atmosphere. In the analysis of mixtures rich in combustible constituents, however, the constituents being determined make such a large proportion of the total, and so much carbon dioxide may be produced, that the correction may have to be applied in precise work.

The foregoing data indicate that when the slow-combustion method of analyses is adopted the true molecular volumes should be used when necessary in calculating the results of analyses of natural gas and other mixtures which contain a high proportion of combustible gases, and that they should also be used when necessary in slow-combustion analyses of prepared combustible gases that are being examined for purity.

⁵⁸ Gladstone, T. H., and Tribe, Alfred. Work cited, p. 154.

DETERMINATION OF HYDROGEN SULPHIDE IN NATURAL GAS

Hydrogen sulphide is shown qualitatively by means of moist lead acetate paper. If present in a gas mixture, the quantity is determined by absorption in a standard solution of iodine and by titration of the excess of iodine with a standard solution of sodium thio-sulphate.

DETERMINATION OF OXYGEN IN NATURAL GAS

Work at the bureau's laboratory has shown that an analyst may fall into error in attempting to determine the oxygen content of some natural gas if he uses alkaline pyrogallate solution or phosphorus for the absorption.

USE OF ALKALINE PYROGALLATE

Oxygen is completely removed from air when a fresh solution of alkaline pyrogallate is used; it can be removed in 2 minutes when the absorption is performed with ordinary Orsat pipettes and the gas mixture is passed back and forth between the burette and pipette to keep the glass rods in the latter covered with fresh solution. This procedure was followed in an attempt to determine the oxygen content of natural gases having the following known compositions:

Composition of natural gases tested for oxygen

Constituents	No. 1	No. 2	No. 3
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
CO ₂	0.03	0.03	0.37
O ₂	.00	.00	.00
CH ₄	84.00	90.66	64.80
C ₂ H ₆	15.00	7.76	27.28
N ₂	.97	1.55	7.55

The percentages of absorption obtained in alkaline pyrogallate solution were as follows: No. 1, 0.13 per cent; No. 2, 0.15 per cent; No. 3, 0.10 per cent.

A greater absorption in alkaline pyrogallate solution was obtained when natural gas containing higher members of the paraffin series was treated with the solution. The percentages of absorption in alkaline pyrogallate solution were as follows: No. 1, 0.32 per cent; No. 2, 0.36 per cent.

USE OF PHOSPHORUS

A large enough proportion of the higher-paraffin hydrocarbons in a gas mixture prevents oxidation of phosphorus by oxygen, which

may be present in the mixture. To illustrate this, a mixture of air and natural gas which contained the following constituents was used:

Constituents of mixture of air and natural gas

Constituents:	Per cent
CO ₂	0.21
CH ₄	39.00
C ₂ H ₆	37.79
Air	23.00

When this mixture was passed into a pipette containing phosphorus, no reduction in volume of the mixture occurred, even after 1 hour's contact at 20° C. Winkler⁵⁹ has called attention to the fact that petroleum vapor prevents the oxidizing action of oxygen on phosphorus. A natural gas that did not contain such a large proportion of the higher paraffins did not prevent this oxidizing action. This gas had the following composition:

Composition of natural gas with small proportion of higher paraffins

Constituents:	Per cent
CO ₂	0.10
CH ₄	82.00
C ₂ H ₆	16.40
N ₂	1.50

Various percentages of air were mixed with this gas and removal of the oxygen with phosphorus was attempted. Oxidation was found to be always complete after 10 minutes. In other words, the action was greatly retarded. The gas mixture had to be passed back and forth between the burette and pipette. The reaction was not complete when the gas mixture was simply passed into the pipette and allowed to stand there.

As explained elsewhere, the analyses of natural gas cited in this work do not show the proportion of higher-paraffin hydrocarbons present in the mixtures; only an indication is given by the proportion of methane and ethane present.

IMPORTANCE OF DETERMINING OXYGEN

The determination of oxygen in natural gas is important because of the statement sometimes made that natural gas used for city consumption may contain air that has leaked into the pipe lines at the compressing stations which force the gas to points of consumption. Natural gas that issues under very high pressure and is trans-

⁵⁹ Winkler, Clemens, Handbook of technical gas analysis. 2d Eng. ed., trans. by George Lunge, 1902, p. 69.

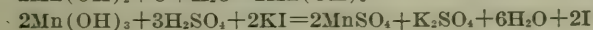
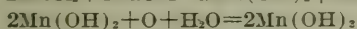
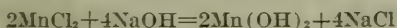
ported through pipe lines does not, however, seem to contain enough higher-paraffin hydrocarbons to affect materially the accuracy of an analysis for oxygen, if alkaline pyrogallate solution is used for the determination of oxygen and if absorptions of 0.20 per cent or under are disregarded as being due to slight absorption of paraffins.

The Bureau of Mines has not detected in the natural gas used in Pittsburgh oxygen in quantities exceeding the error of the apparatus used, although it has been making analyses of the gas for 17 years. The error has never been over 0.20 per cent. Neither has the bureau positively identified oxygen in quantities exceeding the experimental error, in samples received from the wells. The authors can not say that oxygen never exists in gas mains, but they have known of gas mains in a declining field, where the gas was being pumped, to contain considerable air.

MANGANOUS HYDROXIDE METHOD

Because alkaline pyrogallate solution and phosphorus are unsatisfactory for the determination of oxygen the authors have adopted a method used by Phillips⁶⁰ for qualitative testing for oxygen and suggested by him for quantitative determination. The method, which is a modification of that of Winkler for the determination of dissolved oxygen in water, is based on the use of precipitated manganous hydroxide in water. Manganous hydroxide, which is white, absorbs oxygen strongly and changes to manganic hydroxide, which is brown. When a little potassium iodide solution and then sulphuric acid are added, the oxide of manganese redissolves, liberating iodine, which is recognizable by its color, even when only the most minute traces of oxygen are present. By means of a standard solution of sodium thiosulphate the free iodine may be determined.

The reactions taking place in the process and data required for the calculation follow:



Hence, 32 grams of oxygen are equivalent to 507.68 grams of iodine. In using N/40 sodium thiosulphate solution for the estimation of the liberated iodine, 1 c. c. of the solution is equivalent to 1.397 c. c. of oxygen measured at 0° C. and 760 mm. pressure; or 1 c. c. of the solution is equivalent to 0.14 per cent of oxygen in a gas mixture, if only 100 c. c. of the sample is taken for the determina-

⁶⁰ Phillips, F. C., Researches upon the phenomena of oxidation and chemical properties of gases: *Am. Chem. Jour.*, vol. 16, 1894, p. 358.

tion. If larger quantities of the sample are used, the delicacy of the test is much increased.

ANALYSIS OF SMALL SAMPLE

The following scheme is used in the analysis by the authors when only a small quantity, say 100 c. c. of sample, is available for the test: Draw about 15 c. c. of a 10 per cent solution of sodium hydroxide and 25 c. c. of a 10 per cent manganese chloride solution into a 150-c. c. burette with a 100-c. c. bulb at the top. Then draw 100 c. c. of the gas sample into the burette and shake for about 15 minutes with the solutions. Prolonged contact between the gas mixture and the solutions is essential for complete oxidation. Draw a few cubic centimeters of a 10 per cent solution of potassium iodide and 5 per cent sulphuric acid solution into the burette. Transfer the mixture to a flask and titrate immediately with the sodium thiosulphate solution.

When large quantities of the sample are available for the test, bubble the gas mixture slowly through the solutions of sodium hydroxide and manganese chloride. The rate should not exceed 5 c. c. of gas per minute, and at least three solutions should be used to insure a quantitative test.

The following analyses show the results of some experimental work performed by the authors with this method:

Analyses to test the manganous hydroxide method

Oxygen taken, c. c.	Oxygen found, c. c.
0.84-----	0.76
.90-----	.85
.21-----	.24

HEATING VALUE OF NATURAL GAS

In calculating the heating value of natural gas, the values given in the following table are used:

Table of heats of combustion of gases and vapors

Gas	For- mula	Molec- ular weight	Weight at 0° C. and 760 mm. Hg		Authority	Gram calories per gram	B. t. u. per pound	Authority	B. t. u. per cubic foot at 0° C. and 760 mm. Hg		B. t. u. per cubic foot at 60° F. and 29.92 inches Hg		Remarks
			Grams per liter	Pounds per cubic foot					Gross	Net	Gross	Net	
Acetylene	C ₂ H ₂	26.02	1.1707	0.07308	Leduc	11,916	21,449	Thomsen	1,567	1,518	1,483	1,437	Mean gram calories used. Gases at 18° C. or 64.8° F. Thomsen's Thermochemis- cher Untersuchungen, 1906.
Benzol	C ₆ H ₆	78.05	3.4559	.21760	Calculated	10,096	18,173	Stohmann	3,954	3,808	3,741	3,603	Do.
Butane	C ₄ H ₁₀	58.08	2.5985	.16221	Frankland	11,832	21,298	Thomsen	3,455	3,211	3,269	3,038	Do.
Butylene	C ₄ H ₈	56.06	2.5038	.15629	Calculated	11,606	20,891	do	3,270	3,038	3,089	2,875	Do.
Isobutylene	C ₄ H ₈	56.06	2.5038	.15629	do	11,624	20,923	do	3,270	3,075	3,094	2,909	Do.
Carbon	C	12.00				8,080	14,544	do					
Carbon to CO						2,417	4,325	Fauvre & Silberman					
Carbon monoxide	CO	28.00	1.2503	.07805	Rayleigh	2,427	4,369	Thomsen	341	341	323	323	Do.
Ethane	C ₂ H ₆	30.05	1.3567	.08469	Baume & Perrot	12,328	22,190	do	1,879	1,731	1,778	1,638	Do.
Ethylene	C ₂ H ₄	28.03	1.2519	.07815	Calculated	11,893	21,407	do	1,673	1,575	1,583	1,491	Do.
Hydrogen	H ₂	2.016	1.09998	.00562	Rayleigh	33,836	61,085	do	343	294	325	279	Do.
Hydrogen sul- phide	H ₂ S	34.09	1.5352	.09608	Baume & Perrot	4,010	7,218	do	694	645	657	610	Do.
Methane	CH ₄	16.03	.7168	.04475	do	13,221	23,798	do	1,065	967	1,008	916	Do.
Pentane	C ₅ H ₁₂	72.10	3.2197	.20008	Calculated	11,751	21,152	do	4,251	3,939	4,022	3,745	Do.
Pentylene	C ₅ H ₁₀	70.08	3.1300	.19538	do	11,524	20,743	do	4,053	3,809	3,885	3,604	Do.
Propane	C ₃ H ₈	44.06	1.9680	.12285	do	12,011	21,620	do	2,656	2,461	2,513	2,329	Do.
Normal propy- lene	C ₃ H ₆	42.05	1.8781	.11724	do	11,718	21,092	do	2,473	2,327	2,340	2,202	Do.
Trimethylene	C ₃ H ₆							do					Do.
Sulphur	S	32.06				11,877	21,379	do	2,506	2,360	2,371	2,233	
Telol	C ₂ H ₅	92.06	4.1116	.25665	do	2,217	3,991	do	4,689	4,494	4,436	4,251	Do.
Methyl alcohol	C ₂ H ₅ OH	32.03	1.4305	.08930	Stohmann	10,150	18,270	Thomsen	4,689	4,494	4,436	4,251	Do.
Ethyl alcohol	C ₂ H ₅ OH	46.05	2.0567	.12839	do	6,688	10,238	do	1,709	1,563	1,617	1,479	Do.
Hexane (di- isopropyl)	C ₆ H ₁₄	86.11	3.8454	.24004	do	7,384	13,309	do	5,014	4,668	4,744	4,417	Do.
Heptane	C ₇ H ₁₆	100.13	4.4722	.27917	do	11,604	20,887	Luginin	5,715	5,325	5,407	5,038	Heating value of the liquid.

Calculated weight of gas per liter = $\frac{\text{molecular weight of gas}}{\text{molecular weight of oxygen} \times 32.00} \times 1.4292$.

Pound per cubic foot = $\frac{\text{grams per liter} \times 28.315}{433.598}$.

B. t. u. per pound = Gram calories per gram $\times 1.8$. B. t. u. at 60° F. and 29.92 inches Hg = B. t. u. at 0° C. and 760 mm.

B. t. u. per cubic foot = Net B. t. u. per pound.

18.02 $\times H_2 \times 970.4$ = A.
2.02 $\times H_2 \times 970.4$ = A.
molecular weight

Net B. t. u.: $\frac{491.6}{519.6} = .94611$ Hg $\times \frac{491.6}{519.6}$.

LIQUEFACTION AND FRACTIONATION OF NATURAL GAS

The authors have made some laboratory experiments on the liquefaction and fractionation of natural gas. The apparatus (Pl. VIII, p. 75) used consisted of a Töpler mercury pump by means of which vessels could be exhausted of their contained gases, and the gases trapped, measured, and analyzed; Dewar vessels for maintaining liquids at low temperatures for hours; gas-analysis apparatus; specially designed glass gas containers; and liquid air and solid carbon dioxide for obtaining low temperatures.

NATURAL GAS USED AT PITTSBURGH

The first experiments were made with the natural gas used at Pittsburgh, Pa. This gas, as shown by combustion analyses at the time the fractionation experiments were recorded, contained 79.2 per cent of methane, 19.6 per cent of ethane, and 1.2 per cent of nitrogen. The percentage probably includes some of the other inert rare gases, such as helium.⁶¹

FRACTIONATION OF PARAFFINS

As stated before, the analyses by combustion show only the two predominating paraffins. The authors attempted to separate the paraffins in the gas mixture by liquefaction and fractional distillation, as follows: About 90 or 100 c. c. of the gas was introduced into a previously exhausted glass vessel of about 100-c. c. capacity, and the vessel was immersed in liquid air in a Dewar flask. After 10 or 15 minutes the glass vessel, still immersed in liquid air, was connected to a Töpler pump and as much gas as possible was pumped off. The container was then removed from the Dewar flask, allowed to come to room temperature, and the residual gas collected. The first fraction was again liquefied, and as much gas as possible pumped off at the temperature of liquid air. The container was then again removed and allowed to come to room temperature, and the residual gas was added to the residual gas from the first operation. The fractions were then analyzed by the slow-combustion method. All measurements were made over mercury.

By this method of fractionation, methane can be completely separated from the other homologues in a gas mixture, as the vapor pressures of the paraffins higher than methane are almost zero at the temperature of liquid air (-190° C.). To separate the methane completely, a second liquefaction and fractional distillation was employed, the process being outlined above.

⁶¹ Rogers, G. S., Helium-bearing natural gas; U. S. Geol. Survey, Prof. Paper 121, 1921, pp. 28-29. Shepherd, Martin, and Porter, Frank, An improved method for the separation of gas mixtures: Jour. Ind. Eng. Chem., vol. 15, 1923, pp. 1143-1146.

The boiling points of ethane (-93° C.), propane (-45° C.), and butane (1° C.) lie so close together that a clean separation of those constituents is not easily made. At any temperature at which all the ethane can be removed by means of the mercury pump the vapor pressure of the propane is so great that part of the propane is removed also. However, after the separation of the methane at the temperature of liquid air such a temperature can be realized that all of the ethane and part of the propane can be obtained in one fraction, and the remainder of the propane and all of the butane can be collected in the second fraction. According to Lebeau and Damiens,⁶² the optimum temperature at which all the ethane and part of the propane can be separated from the remainder of the propane and all the butane is -130° C. After the first fraction has been removed, the vessel containing the residual gas is removed from the Dewar flask containing the refrigerant, and the remainder of the propane and all of the butane in this second fraction are collected at normal temperatures by means of the mercury pump.

After the fractions are collected they can be analyzed by the slow-combustion method, as each contains only two constituents. The composition of the mixture will then be accurately known.

If gaseous paraffin hydrocarbons and the vapors of liquid hydrocarbons exist in a mixture, separation of the gaseous paraffins can be made from the vapors of the liquid paraffins by subjecting the mixture to a temperature of -100° C., when the gaseous constituents can be collected by means of the mercury pump (Pl. VIII), the vapors of the liquid paraffins being left behind. The condensed vapors can then be recovered by allowing them to evaporate at room temperatures. Such mixtures are found in casing-head gases and gases drawn from the earth under reduced pressure in connection with the manufacture of gasoline from natural gas.

CONSTITUENTS OF PITTSBURGH NATURAL GAS

By using the above method for determining the percentage of the various constituents in the natural gas used at Pittsburgh, the following results were obtained:

Comparison of data obtained in fractionation tests

Constituents	Experiment No.—			
	1	2	3	4
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Methane.....	87.1	87.0	86.3	86.6
Nitrogen.....	1.4	1.2	1.2	1.6
Ethane.....	5.0	5.8	6.5	5.7
Propane.....	6.5	6.0	6.0	6.1
Total.....	100.0	100.0	100.0	100.0

⁶² Lebeau, P., and Damiens, A., Sur une méthode d'analyse des mélanges d'hydrogène et d'hydrocarbures saturés gazeux; mélanges complexes: *Compt. rend.*, t. 156, No. 4, 1913, p. 325.

These analyses show fair agreement among themselves. The greatest discrepancy is in the ethane and propane content, principally because of the difficulty encountered in exactly analyzing a small sample of either of these two gases. By taking larger samples of the original gas, however, this difficulty may be overcome.

There still remains the possibility of the presence of butane in the natural gas. By the method outlined above methane alone can be separated from the other homologues, as its boiling point lies 67° C. from that of ethane, the next higher hydrocarbon.

The boiling point of ethane, however, differs from that of propane by only 48° C., and the boiling point of propane differs from that of normal butane by 44° C.; consequently, no sharp separation can be made by the above method for ethane, propane, and butane, but such a temperature can be utilized that after separation of the methane from the other paraffins at -190° C. all the ethane and part of the propane can be obtained in one fraction and the remainder of the propane and all the butane can be collected in the second fraction. This temperature is -130° C. The authors subjected residual fractions (paraffins higher than methane) from the natural gas of Pittsburgh to this temperature, and by means of the mercury pump removed as much of the gas as possible. The removed fraction was found to consist of ethane and propane and the residual fraction of propane only.

TEST FOR GASOLINE CONTENT OF NATURAL GAS

As a result of the condensing of certain paraffin hydrocarbons in a natural-gas mixture and the use of the resultant liquid as gasoline, a demand has arisen for a test that will show the amount of liquid obtained per unit volume of natural gas at definite pressures and temperatures. Since by present procedure it is impossible to determine the separate paraffins in a mixture, the demand has been met in part by determining the density of the gas and dissolving the gas in a solvent that has a greater solvent action on the higher than on the lower paraffin hydrocarbons. Claroline oil, olive oil, and paraffin oil have been used.⁶³

The solubility test is not quantitative because all of the dissolved constituents represent the gasoline to be obtained in actual practice, and because certain paraffins are dissolved to the entire exclusion of the others. Even methane is soluble to some extent in the solvents named, but the higher paraffin hydrocarbons are much more soluble;

⁶³ Burrell, G. A., and Jones, G. W., Methods of testing natural gas for gasoline content: Tech. Paper 87, Bureau of Mines, 1916, 26 pp.

consequently, it is assumed that under the same conditions of plant operation the natural gas that is most soluble will produce the most gasoline.

RELATIVE EFFECTS OF SOLVENTS

To determine the relative solvent effects, the authors have subjected some samples of natural gas to solution in different oils. The

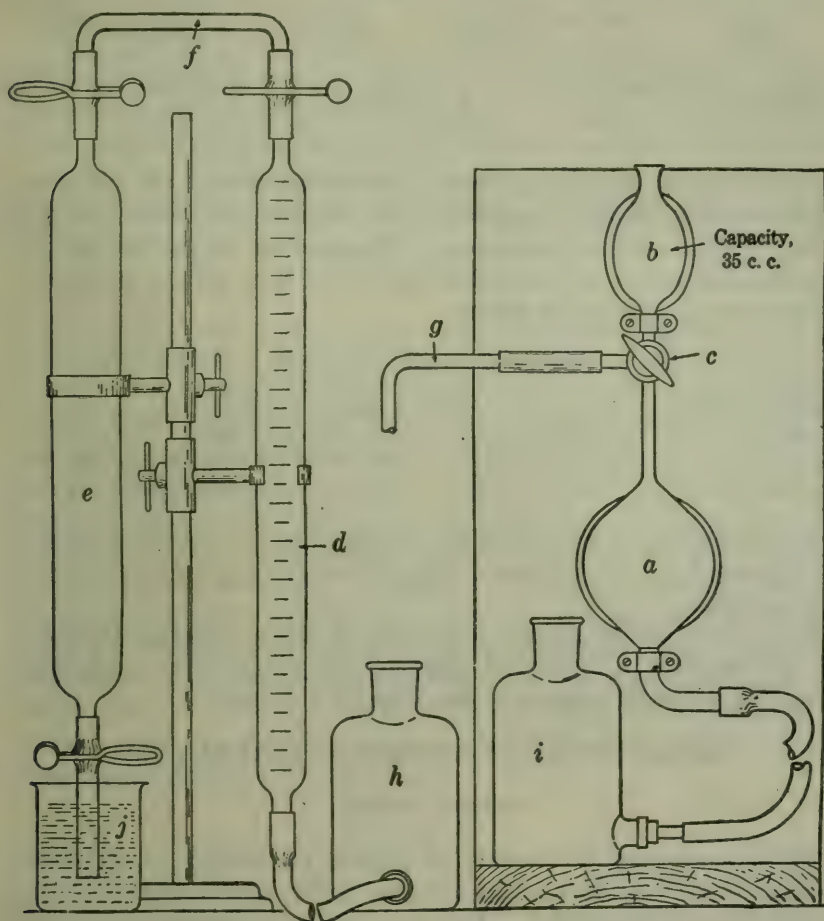


FIGURE 27.—Apparatus for determining the solubility of natural gas in oil

following table shows the solubility in several varieties of oil of Pittsburgh natural gas, at a temperature of 20° C. The specific gravity of the gas as compared to air is 0.63 at 0° C. and 760 mm. pressure. It is not adapted to the commercial production of gasoline, but was used to show the solvent action mentioned before.

In making a test, 35 c. c. of the oil was placed over mercury in a Hempel pipette (fig. 27), and was shaken for about 3 minutes with 100 c. c. of the gas until there was no further reduction in volume of the gas.

Results of tests of solubility of the natural gas used at Pittsburgh in different oils

Oil used	Character of oil	Solubility, per cent	Oil used	Character of oil	Solubility, per cent
Claroline.....	Mineral.....	15.5	Olive.....	Vegetable.....	13.7
Russian white.....	do.....	16.4	Rapeseed.....	do.....	14.7
Sperm.....	Animal.....	16.5	Cottonseed.....	do.....	14.8

The above determination could be checked within 0.5 per cent. Considerable uniformity regarding the solubility of the natural gas in the different oils will be noticed. The claroline oil had the following characteristics, as determined by I. C. Allen, former petroleum chemist of the Bureau of Mines:

Characteristics of claroline oil

Specific gravity.....	0.8667 at 15° C.
Viscosity.....	4.4° Engler at 20° C.
Flash point.....	152° C., Pensky-Martens, closed test.
Ignition point.....	270° C., Pensky-Martens, closed test.

The solubility of pure methane in claroline is 11.0 per cent and in cottonseed oil 9.5 per cent. The solubility of pure ethane oil is 68.5 per cent.

It was found that results equivalent to those obtained from the use of claroline oil could be obtained by using 50 c. c. of ethyl alcohol in the same manner as claroline oil was used.

DETERMINATION OF DENSITY OF NATURAL GAS

WEIGHT METHOD

Determination of the density of natural gas consists in weighing the gas in a globe of known capacity under definite conditions of temperature and pressure. The globe used is a spherical glass bulb sealed to a capillary glass stopcock that has been worked very carefully. To eliminate errors due to changes in the atmospheric temperature and pressure and consequently to change in the buoyancy of the globe, a closed bulb having the same external volume as the density globe is used as a counterpoise during the weighing. The capacity of the globe is determined at about 16° C.

The globe is first thoroughly cleaned and dried and the stopcock lubricated, care being taken to keep the hole in the plug free from grease; the globe is then exhausted and weighed. After the globe is weighed it is filled with boiled water and suspended in a basin of water for 15 minutes at constant temperature. After the temperature has been observed and the stopcock closed the water is removed from the capillary tube above the tap and the bulb carefully dried and suspended from the balance for the second weighing. The authors use a 100-c. c. bulb.

For a rapid and approximate determination of the density of different kinds of natural gas, Bunsen's effusion method can be used, whereby a given quantity of the gas is allowed to flow through a small aperture. The time taken by a like quantity of air in passing is a measure of the density of the gas. The specific gravities of gases are inversely proportional to the squares of their rates of effusion.

CALCULATION

The density of a natural gas may also be calculated from its chemical analysis. The different percentages of the constituents found are multiplied by their densities as compared to air, and the sum of these values divided by 100. The following table gives the values used at the Pittsburgh station of the Bureau of Mines for the calculation of the densities of natural gases. The values obtained by this method are on a dry gas basis. To correct for the moisture content present the percentage of moisture in the gas must be determined; then the percentages of gases found by analysis must be recalculated to include the water vapor present. The density is then calculated from the corrected gas analysis, as given before. The water-vapor content seldom exceeds 2 per cent, and since the density of water does not differ much from that of the majority of natural gases, the dry gas analysis may ordinarily be used for calculating the density of a gas.

Table of gas densities ^a

Gas	Molecular weight ^b	Weight per liter in grams at 0° C. and 760 mm. ^c	Specific gravity air=1 ^d	Authority
Acetylene (C ₂ H ₂)	26.02	1.1791, observed	0.9121, observed	Stahrfoss, Jour. Chim. Phys., t. 16, 1918, p. 175.
Ammonia (NH ₃)	17.06	0.7708, observed	0.5962, observed	Guye, Chem. Ztg., Jahrg. 36, 1912, p. 402.
Butane (C ₄ H ₁₀)	58.08	2.5985, observed	2.0100, observed	Frankland, Ann. Chem. Pharm., vol. 71, 1849, p. 171.
Butylene (C ₄ H ₈)	56.96	2.5036, calculated	1.9366, calculated	Calculated.
Carbon dioxide (CO ₂)	44.00	1.9768, observed	1.5291, observed	Rayleigh, Proc. Royal Soc., vol. 62, 1897, p. 204.
Carbon monoxide (CO)	28.00	1.2504, observed	0.9672, observed	Do.
Chlorine (Cl ₂)	70.92	3.214, observed	2.486, observed	Jacqueroed, Journ. Chim. Phys., t. 11, 1913, p. 269.
Ethane (C ₂ H ₆)	30.05	1.3565, observed	1.0493, observed	Stahrfoss, Jour. Chim. Phys., t. 16, 1918, p. 175.
Ethylene (C ₂ H ₄)	28.03	1.2603, observed	0.9748, observed	Batuecas, Jour. Chim. Phys., t. 16, 1918, p. 322.
Fluorine (F ₂)	38.0	1.697, observed	1.3127, observed	Moissan, Compt. rend., t. 138, 1904, p. 728.
Hydrobromic acid (HBr)	80.93	3.6443, observed	2.8190, observed	Moles, Jour. Chim. Phys., t. 15, 1917, pp. 464-465.
Hydrochloric acid (HCl)	36.47	1.6398, observed	1.2684, observed	Guye, Jour. Am. Chem. Soc., vol. 30, 1908, p. 43.
Hydrogen (H ₂)	2.016	0.0899, observed	0.0695, observed	Morley, Smithsonian Inst., 1895.
Hydrogen sulphide (H ₂ S)	34.09	1.5392, observed	1.1906, observed	Baumé and Perrot, Jour. Chim. Phys., t. 6, 1908, p. 610.
Methane (CH ₄)	16.03	0.7168, observed	0.5545, observed	Baumé and Perrot, Jour. Chim. Phys., t. 7, 1909, p. 369.
Methyl chloride (CH ₃ Cl)	50.48	2.3045, observed	1.7826, observed	Baumé, Jour. Chim. Phys., t. 6, 1908, pp. 1-90.
Methyl ether ((CH ₃) ₂ O)	46.05	2.1096, observed	1.6318, observed	Do.
Nitric oxide (NO)	30.01	1.3402, observed	1.0367, observed	Guye and Pavila, Mem. Soc. Phys. et Hist. Nat. de Geneva, t. 35, 1908, p. 648.
Nitrous oxide (N ₂ O)	44.02	1.9777, observed	1.5228, observed	Guye, Jour. Am. Chem. Soc., vol. 30, 1908, p. 143.
Nitrogen (N ₂)	28.02	1.2507, observed	0.9674, observed	Rayleigh, Proc. Royal Soc., vol. 62, 1897, p. 204.
Oxygen (O ₂)	32.00	1.4291, observed	1.1054, observed	Guye, Pintza, Germann, Morley, Leduc, and Rayleigh. Calculated.
Pentane (C ₅ H ₁₂)	72.09	3.2194, calculated	2.4902, calculated	Do.
Pentylene (C ₅ H ₁₀)	70.08	3.1297, calculated	2.4203, calculated	Timmermans, Jour. Chim. Phys., t. 18, 1920, p. 133.
Propane (C ₃ H ₈)	44.06	2.0200, observed	1.5625, observed	Calculated.
Propylene (C ₃ H ₆)	42.05	1.8779, calculated	1.4526, calculated	Germann and Booth, Jour. Phys. Chem., vol. 21, 1917, pp. 81-100.
Silicon tetrafluoride (SiF ₄)	104.3	4.6840, observed	3.6232, observed	Jacqueroed and Pintza, Mem. Soc. Phys. et Hist. Nat. de Geneva, t. 35, 1908, p. 592.
Sulphur dioxide (SO ₂)	64.07	2.9266, observed	2.2638, observed	Guye, Jour. Chim. Phys., vol. 15, 1917, p. 561.
Water vapor (H ₂ O)	18.02	0.8048, calculated	0.6997, calculated	Guye, Jour. Chim. Phys., vol. 5, 1907, p. 203.
Air		1.2928, observed		Taylor, Phys. Rev., vol. 10, 1917, p. 653.
Argon (A)	39.88	1.7809, observed	1.3766, observed	Moore, Jour. Chem. Soc., vol. 93, 1908, p. 2181.
Helium (He)	3.99	0.1785, observed	0.1381, observed	Leduc, Compt. rend., t. 158, 1914, p. 864.
Krypton (Kr)	82.9	3.7063, observed	2.8669, observed	Moore, Jour. Chem. Soc., vol. 93, 1908, p. 2181.
Neon (Ne)	20.2	0.9000, observed	0.6962, observed	
Xenon (X)	130.2	5.837, observed	4.515, observed	

^a This table was adopted by the chemical section of the Pittsburgh experiment station of the Bureau of Mines in January, 1921.

^b Molecular weights as taken, oxygen=32.

^c Weight of gases per liter at 0° C. and 760 mm. were obtained by the following formula: The calculated weight of gas per liter = $\frac{\text{molecular weight of gas}}{\text{molecular weight of oxygen}=32} \times 1.4291$

^d Specific gravity of gas (air=1) = weight of gas per liter divided by 1.2928.

PROPERTIES OF THE MORE COMMON PARAFFIN HYDROCARBONS

Because of the increased interest taken in natural gas and in gasoline from the natural-gas industry, the authors have compiled from various sources the following table showing the properties of the more common paraffin hydrocarbons:

Properties of gaseous and some liquid paraffins

Name	Formula	Boiling point, °C. ^a	Name	Formula	Boiling point, °C. ^a
Methane.....	CH ₄	-160	Pentane.....	C ₅ H ₁₂ ...	36.4
Ethane.....	C ₂ H ₆	-93	Hexane.....	C ₆ H ₁₄ ...	68.9
Propane.....	C ₃ H ₈	^b -45	Heptane.....	C ₇ H ₁₆ ...	98.4
Butane.....	C ₄ H ₁₀ ...	1			

^a Holleman, A. F., Organic chemistry. Edited by A. J. Walker, 1910, p. 41.

^b Other authorities give -17° C.

Properties of the gaseous and some of the liquid paraffins

Name	Illuminating value	Liquefaction point (critical constants)	Calculated volume of gas (at 60° F. and 30 inches pressure) from 1 gallon	Theoretical volume of air necessary to burn 1 cubic foot of gas
	<i>British candle-power</i>		<i>Cubic feet</i>	<i>Cubic feet</i>
Methane.....	^a 5.0	-95.5° C. at 735 ^b -81.8° C. at 807 ^c		9.57
Ethane.....	^b 35.0	35° C. at 664 ^b	53	
Propane.....	^d 53.9	97° C. at 647 pounds ^c	45	23.92
Butane.....			37	31.10
Pentane.....			31	38.28
Hexane.....			27	

^a Wright, L. T., Jour. Chem. Soc., vol. 47, 1885, p. 200.

^b Landolt, H., and Börnstein, R., Physikalisch-chemische Tabellen. 1905, pp. 182-185 (by Dewar).

^c Landolt, H., and Börnstein, R. Work cited, pp. 182-185 (by Olszewski).

^d Frankland, P., Jour. Chem. Soc., vol. 47, 1885, p. 235.

SUMMARY

The apparatus and methods described in this bulletin have proved suitable for the analysis of gas mixtures containing the constituents usually determined in gas analysis. The apparatus shown in Plate III is especially adapted for making a complete and accurate analysis of mixtures containing very small proportions of some constituents. The range of work possible with the apparatus is limited by the capacity of the stem of the burette, which is purposely made small so that successive graduations may mean very small differences in volume. Gas mixtures containing large percentages of such constituents as methane, hydrogen, and carbon monoxide are analyzed with the apparatus shown in Figure 10. For such mix-

tures an apparatus as accurate as that shown in Plate III is seldom necessary. With these two types of apparatus the authors perform most of the eudiometric analyses in connection with their investigations for the Bureau of Mines, whose gas laboratory makes over 400 determinations a month.

The other apparatus illustrated in this bulletin are modifications of these two types and are designed for special work. Mining companies, for example, are chiefly interested in the methane content of mine air, or in the amount of methane and carbon dioxide therein. A particular ventilation study may frequently require a large number of analyses for carbon dioxide and oxygen.⁶⁴

Laboratories at industrial plants not infrequently are content to sacrifice speed in the endeavor to make more accurate determinations of industrial gases than can be made with the ordinary technical forms of apparatus designed for use with water in the burette and combustion pipette. The apparatus shown in Figure 11 is adapted for such work, and is also suitable for a large variety of experimental work. For analyses of natural gas, which constitute the gas analyses made in connection with some investigations, the apparatus shown in Figure 12 has been stripped of unnecessary pipettes, as shown in Figure 26. In designing apparatus for special work a reduction in the number of parts has been sought, because needless parts involve complications.

An attempt was made to assemble precise apparatus for exact work in experimental and other laboratories, as well as simpler apparatus for field work and for use by mining men who are not very familiar with apparatus for gas analysis. For instance, the authors have found that men entirely unfamiliar with such apparatus have done good work with the apparatus shown in Figures 7, 8, and 9 after a little instruction.

PUBLICATIONS ON ANALYSIS OF MINE GASES

Requests for publications available for free distribution should be addressed to the Director, Bureau of Mines.

The Bureau of Mines issues a list showing all its free publications that are available for distribution as well as those obtainable only from the Superintendent of Documents, Government Printing Office. Interested persons should apply to Director, Bureau of Mines, for a copy of the latest list.

PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION

TECHNICAL PAPER 357. A critical study of the Burrell indicator for combustible gases in air, by Lowell H. Milligan. 1924. 40 pp.

⁶⁴ Burrell, G. A., and Seibert, F. M., Apparatus for gas-analysis laboratories at coal mines: Tech. Paper 14, Bureau of Mines, 1913, p. 7.

TECHNICAL PAPER 373. The pyrotannic acid method for the quantitative determination of carbon monoxide in blood and in air, by R. R. Sayers and W. P. Yant. 1925. 18 pp., 2 pls., 1 fig.

**PUBLICATIONS OBTAINABLE ONLY FROM THE SUPERINTENDENT
OF DOCUMENTS**

BULLETIN 42. The sampling and examination of mine gases and natural gas, by G. A. Burrell and F. M. Seibert. 1913. 116 pp., 2 pls., 23 figs. 20 cents.

BULLETIN 105. Black damp in mines, by G. A. Burrell, I. W. Robertson, and G. G. Oberfell. 1916. 88 pp. 10 cents.

TECHNICAL PAPER 11. The use of mice and birds for detecting carbon monoxide after mine fires and explosions, by G. A. Burrell. 1912. 16 pp. 5 cents.

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TECHNICAL PAPER 39. The inflammable gases in mine air, by G. A. Burrell and F. M. Seibert. 1913. 24 pp., 2 figs. 5 cents.

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TECHNICAL PAPER 121. Effects of temperature and pressure on the explosibility of methane-air mixtures, by G. A. Burrell and I. W. Robertson. 1916. 14 pp., 3 figs. 5 cents.

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TECHNICAL PAPER 185. Use of the interferometer in gas analysis, by F. M. Seibert and W. C. Harpster. 1918. 18 pp., 1 pl., 5 figs. 5 cents.

TECHNICAL PAPER 190. Methane accumulations from interrupted ventilation, by H. I. Smith and R. J. Hamon. 1918. 46 pp., 2 pls., 5 figs. 10 cents.

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